VOL. XXII. 1912

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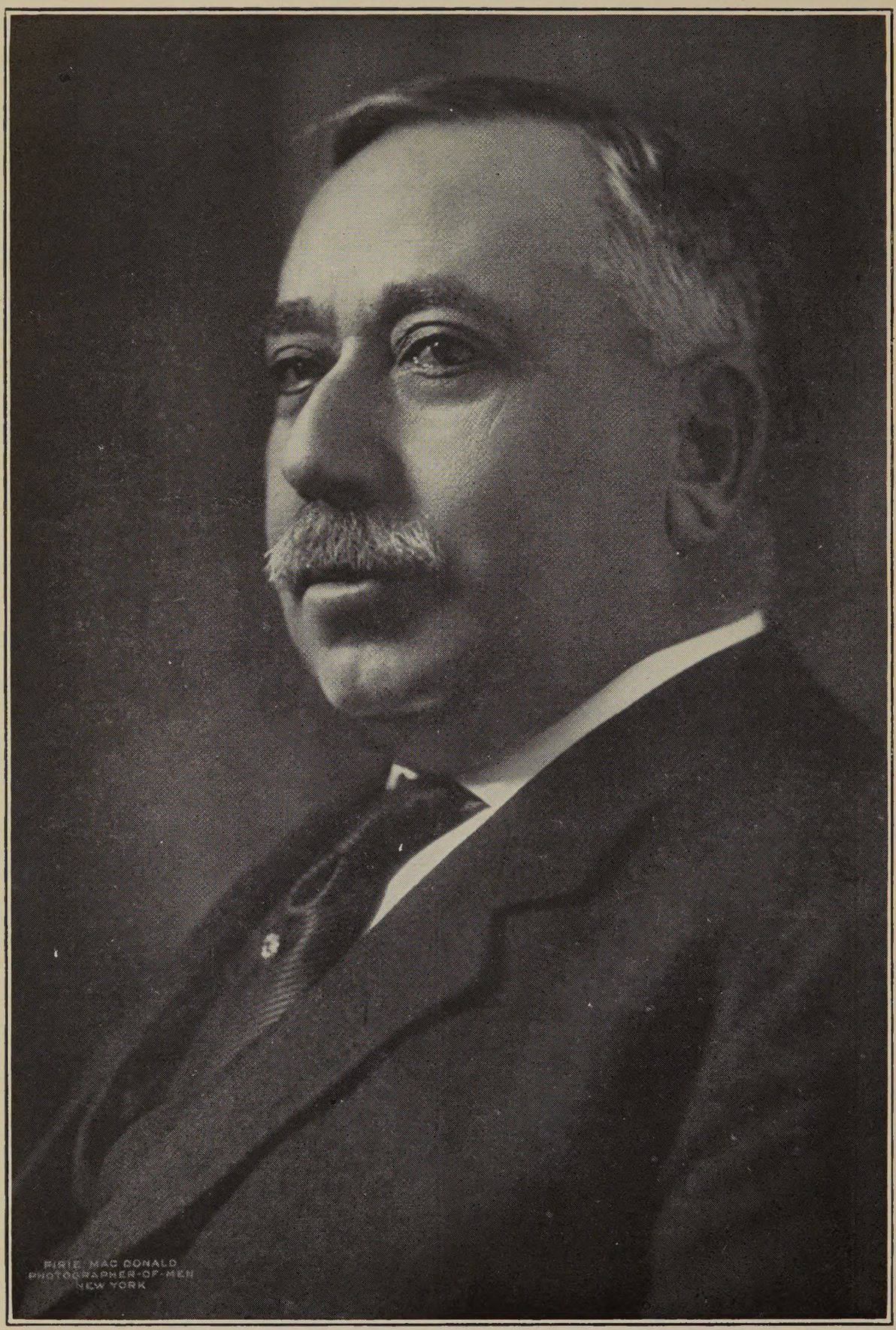
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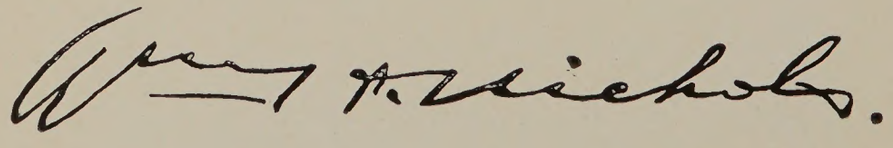

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TRANSACTIONS

OF THE

AMERICAN

ELECTROCHEMICAL SOCIETY

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VOLUME XXII

TWENTY-SECOND GENERAL MEETING

NEW YORK CITY, SEPT. 7, 9, 10, 1912

HELD IN JOINT SESSION WITH

THE VIIIth INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

SECTION: "ELECTROCHEMISTRY"

PUBLISHED BY

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LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.

1913

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VOLUME XXII. 1912.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE TWENTY-SECOND GENERAL MEETING OF THE SOCIETY, HELD IN NEW YORK CITY, IN CONJUNCTION WITH THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY AND THE AMERICAN INSTITUTE OF MINING ENGINEERS, SEPTEMBER 7, 9 AND 10, 1912.

Number of members registering, 134; guests, 28; total, 162.

SESSION OF SEPTEMBER 7th

All sessions were held in the Chemical Lecture Room of Havemeyer Hall, Columbia University.

Prof. Charles F. Chandler, of Columbia University, greeted the assembly in the following characteristic manner: "When I see so many chemists gathered together it carries my memory back to the days when there were not as many chemists in the whole United States as there are now in this room; to a time, in fact, when there was no place in the United States where a man could get a chemical education. That is within my recollection. I entered at Harvard University in 1853, fascinated with the idea of being a chemist. I stayed there a year, receiving practically no instruction in chemistry. There were half a dozen others there like myself taken with the idea of becoming chemists, but the only practical instruction we obtained was what we got

from each other. I have often wondered, thinking over that year in the Lawrence Scientific School, whether we have really improved matters by the methods we have now adopted for teaching chemistry. In those days the student had to do the work, and if he had not enough interest in the subject and enough character to do the work, he dropped out and went into something else. Now we open our doors and we take students in by the hundreds who say they want to the chemists—and we do all the work. As a student in Wöhler's Laboratory, in Göttingen, afterwards, I found that we had pretty nearly the same system we had at Harvard, except that our dear old Professor took a personal interest in each one of the students in his laboratory, gave us a superb course of daily lectures, but when it came to laboratory work he never told us what to do. He did not write on the blackboard schemes for qualitative analysis which the student was to take down and follow in the laboratory. He did not put down schemes for an analysis of iron ore, and all the other things that a student has to analyze, so that the student would not be obliged to look in any book; but he came into the laboratory and he said, "Well, Chandler, what are you doing now?" "Well," I said, "Professor, I have recently finished the last piece of work you gave me and I am ready to turn in the results." And I would do it and then he would think a minute. "Well," he would say, "I will give you a piece of thorite; you must make some thorium." He never said a word about how it should be done or what thorite was or anything about it. As a matter of fact I had never heard of thorite or thoria either at that time. That sent me to the library to hunt up the method for decomposing thorite and extracting and purifying the thorium. That was the plan. I don't think that Wöhler in the year that I worked in his laboratory ever told me how to do anything, except in his lectures, when he lectured on general chemistry; but when it came to laboratory work of the students, the student was expected to read up the subject and find out how to do it. That is so radically different from the plan we follow in this country now in teaching students that I often wonder whether we have improved on the old methods. Of course, by our present plan we are able to crowd ever so much more material

into the student than he could possibly get if he had to work it all out himself, and perhaps it is the development of the science, the enormous magnitude and the variety of the field that we have to cover now, that makes the new system necessary."

The session of September 7th was held in conjunction with Sections Xa: Electrochemistry and IIIa: Mining and Metallurgy, of the Congress, and the American Institute of Mining Engineers. The "Topic" of the session was "Electrometallurgy." Prof. Wm. H. Walker, President of Section Xa, called the meeting to order at 10 A. M., and invited President W. Lash Miller, of this Society, to the Chair. Prof. Jos. W. Richards, Chairman of Section IIIa, acted as Secretary of the Session.

Papers by F. A. J. FitzGerald, C. H. Vom Baur, A. E. Greene (read by J. W. Richards) and R. Amberg were read and discussed, as printed in full in these Transactions.

SESSIONS OF SEPTEMBER 9th

The sessions of this day were held in conjunction with Sections Xa: Electrochemistry, Xb: Physical Chemistry and II: Inorganic Chemistry, of the Congress.

The morning session was called to order at 10 A. M., President W. Lash Miller of this Society presiding.

Papers by T. W. Richards and F. Daniels, J. H. Hildebrand (2), G. D. Buckner and G. A. Hulett (read by Prof. Hulett) and J. S. Laird and G. A. Hulett (2) (read by Prof. Hulett), were presented and discussed, as printed in full in these Transactions.

The afternoon session was called to order at 1 P. M., Pres. W. Lash Miller in the Chair.

Papers by S. A. Tucker and H. L. Read (read by Prof. Tucker), E. W. Washburn and S. J. Bates (read by Prof. Washburn), and E. Weintraub, were presented and discussed, and, with the exception of the latter, are printed in full in these Transactions. (The substance of Dr. Weintraub's lecture on Boron has already appeared in our Transactions, Vols. **16**, 165, and **18**, 207).

TUESDAY, SEPTEMBER 10th

The morning session was held in conjunction with Sections Xa: Electrochemistry and VIa: Paper, of the Congress.

The meeting was called to order at 10 A. M., Prof. C. F. Burgess, Vice-President of Section Xa, in the Chair.

Papers by W. H. Walker and R. E. Gegenheimer (read by Prof. Walker) and E. Wildermann were read and discussed, as printed in full in these Transactions.

The afternoon session was held in conjunction with Sections IIIa: Mining and Metallurgy, Xa: Electrochemistry and XIb: Conservation. The meeting was called to order at 1 P. M. by Prof. W. H. Walker, President of Section Xa.

Papers by W. N. Lacey, A. Stansfield, D. L. McLeod and J. W. McMahon, W. H. Walker and W. A. Patrick (read by Prof. Walker) and L. Bradley, were presented and discussed, as printed in full in these Transactions.

OTHER SESSIONS OF THE CONGRESS

Papers by W. B. Schulte (read by Prof. C. F. Burgess), H. H. Hanson and W. K. Lewis, J. K. Clement and L. V. Walker (read by Mr. Clement), G. C. Whipple and M. C. Whipple (read by G. C. Whipple), C. F. Burgess and J. Aston (read by Prof. Burgess), J. Aston and C. F. Burgess (read by Prof. Burgess), were presented and discussed at a joint meeting of Sections Xa: Electrochemistry and Ve: Paints and Pigments, of the Congress, on Wednesday morning, September 11th, the "Topic" being "Corrosion of Iron and Steel."

Papers by E. P. Schoch and D. T. Brown (read by Prof. Schoch), E. B. Spear, C. Hambuechen and O. E. Ruhoff (read in abstract by Dr. E. F. Roeber), W. D. Bancroft, L. V. Walker and C. F. Miller (read in abstract by Mr. Baker), were presented and discussed at a meeting of Section Xa: Electrochemistry, on Wednesday afternoon, September 11th.

Papers by C. W. Kanolt, S. A. Tucker and Y. Tsenshan Wang, E. B. Spear, C. Chow and A. L. Chesley, W. D. Bancroft and T. R. Briggs, Utley Wedge, R. C. Wells, W. Palmaer, J. N. Pring and D. M. Fairlie, and C. G. Fink, were read at other sessions of Sections IIIa, Xa and Xb, of the Congress.

The above papers, presented at sessions of Congress Sections not held in conjunction with this Society, are printed in these Transactions because of their importance to the members of this Society, with the kind permission of the International Congress, to whose officials our acknowledgments are hereby made.

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Charles Wirt, 129 Cliveden Ave., Germantown, Phila., Pa.
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James D. Burby, 625 4th Ave., Astoria, L. I., N. Y.

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September 28, 1912.

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YATSEVITCH, Michael (Feb. 23, '12) Instructor in Chemistry, Polytechnical Institute, Kiev, Russia.
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ZIMMERMAN, J. G. (Nov. 6, '02) 622 Otjen St., Milwaukee, Wis
ZWINGENBERGER, Otto K. (Jan. 27, '12) Chemist, Roessler & Hasslacher Chem. Co.; res., 255 High St., Perth Amboy, N. J.

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Beckman, J. W.
Bennie, P. McN.
Bliss, Wm. Lord
Callahan, J. F.
Carveth, H. R.
Cole, E. R.
Converse, V. G.
Corbin, J. Ross
Cox, G. E.
Doerschuk, V. C.
Dunlap, O. E.
Edmands, I. R.
FitzGerald, F. A. J.
Fowler, R. E.
Furness, G. C.
Giles, I. K.
Greene, F. V.
Griffith, J. R.
Hall, C. M.
Hall, S. F.
Harper, J. L.
Haskell, F. W.
Hepburn, D. M.
Hinchley, A. T.
Horry, W. S.
Hooker, A. H.
Hutchins, Otis
Imlay, L. E.
Johnson, J. A.
Kellogg, H. W.
Koethen, F. L.
Lidbury, F. A.
MacMahon, J.
Marsh, C. W.
Marshall, J. G.
Mauran, M.
McCullough, H. F.
Meredith, W. F.
Moritz, C. H.
Moyer, G. C.
Ornstein, G.
Petinot, N.
Phillips, R.
Reeve, A. G.
Rodgers, A. G.
Ross, Wm.
Russell, C. A.
Saunders, L. E.
Sergeant, E. M.

Simmers, A. L.
Smith, E. S.
Smith, W. A.
Snowdon, R. C.
Speiden, E. C.
Sprague, E. C.
Spurge, E. C.
Stamps, F. A.
Stone, G. W.
Taylor, Chas. E.
Tone, F. J.
Vaughn, C. F.
Wallace, W.
Wilson, I. W.
Wilson, J. R.
Williamson, A. M.
Yoe, Harry A.

Ossining—
Acker, Chas. E.

Penn Yan—
Taylor, E. R.

Piermont—
Main, W.

Poughkeepsie—
Moulton, C. W.
Quintard, Edw.

Prince Bay (S. I.)—
Hammond, J. F.
Johnston, F. A.
Johnston, W. A.

Richmond Hill (L. I.)—
Haslwanter, C.
Maeulen, F.
Smull, J. G.

Rochester—
Hutchings, J. T.
Schwarz, R. C.

Schenectady—
Andrews, W. S.
Arsem, W. C.
Arthur, Walter
Capp, J. A.
Coffin, F. P.
Creighton, E. E.
Dushman, Saul
Franklin, M. W.
Hansen, C. A.
Hawkins, L. A.
Lamar, M. O.
Langmuir, I.
Murphy, E. J.
Reist, H. G.
Rushmore, D. B.
Seede, J. A.
Steinmetz, C. P.
Taylor, J. B.
Valentine, I. R.
Van Brunt, C.
Whitney, W. R.
Willey, L. M.

Syracuse—
Brookfield, W. B.
Matthews, J. A.
Pennock, J. D.
Sykes, H. W.

Troy—
Hunter, M. A.
Lincoln, A. T.

Utica—
Johnson, M. H.

Watertown—
Williams, F. M.

Wellsville—
Seabury, R. L.

Yonkers—
Baekeland, L. H.
Harrington, E. I.
Statham, Noel

NORTH CAROLINA.

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Gilchrist, P. S.

Clemmons—
Pickens, Rufus H.

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Betts, A. G.

West Raleigh—
Browne, W. H.

Whitney—
Marseilles, Wm. P.

NORTH DAKOTA.

Agricultural College—
Dolt, Maurice L.

OHIO.

Akron—
Geer, W. C.
Shaw, E. C.

Alliance—
Baily, T. F.

Ashtabula—
Harrar, E. S.

Canton—
Miller, Wm. H.

Cincinnati—
Aston, James

Cleveland—
Brady, W. B.
Brown, J. W.
Brownlee, Edw. G.
Burnell, Arthur W.
Chillas, R. B., Jr.
Clymer, W. R.
Collens, C. L., 2d
Crider, J. S.
Fleming, R.
Fleming, S. H.
Glascock, B. L.
Graves, W. G.
Hamister, V. C. H.
Hill, Chas. W.
Hudson, A. J.
Humel, Edward J.
Hyde, E. P.
Koehler, W.
Mann, W. W.
Ordway, D. L.
Pritz, W. B.
Pulman, O. S.
Smith, A. W.
White, F. L.
Whitlock, E. H.
Woodward, J. M.

Columbus—
Allensworth, H. R.
Flowers, A. E.
Withrow, J. R.

Dayton—
Clements, F. O.
Deeds, E. A.
Dorsey, H. G.
Niswonger, E. E.

Elyria—
Boynton, A. J.
Briggs, F. H.

Fostoria—
Downes, A. C.

Fremont—
Goodwin, J. H.
Ziegler, W. W.

Lakewood—
Mott, W. R.

Middletown—
Ahlbrandt, G. F.
Richardson, E. A.
Napoleon—
Long, Geo. E.
Oberlin—
Crafts, W. N.
Salem—
Davis, D. L.
Steubenville—
Homan, J. G.
Wadsworth—
Snyder, J. L. K.
Youngstown—
Brinker, H. L.
Danforth, Chas. W.

OREGON.

Eugene—
Shinn, F. L.

PENNSYLVANIA.

Altoona—
Casselberry, H.
Walters, H. E.
Aspinwall—
Davis, R. W.
Hessom, B. F., Jr.
Beaver—
Baltzell, W. H.
Cornell, Sidney
Bethlehem—
Landis, W. S.
Brackenridge—
Connell, H. R.
Braddock—
Friedlaender, E.
Lewis, J. D.
Bridgeville—
Clark, W. W.
Saklatwalla, B. D.
Bryn Mawr—
Ely, T. N.
Canonsburg—
Bleecker W. F.
Guerber, A. J.
Chester—
Comey, A. M.
Coatesville—
Coates, J.
Columbia—
Kern, P. E.
Colwyn—
McConnell, J. Y.
Coraopolis—
Stafford, S. G.
Creighton—
Gelstharp, F.
Kerr. Chas. H.
Parkinson, J. C.
Crofton—
Fawcett, L. H.
Driftwood—
Gray, C. W.
Duquesne—
Unger, J. S.
Easton—
Adamson, G. P.
Gordon, C. McC.
Hart, E.
Shimer, E. B.
Economy—
Farnham, F. F.
Edgewood—
Donkin, Wm. A.
Ellwood City—
Barton, Chas. R.
Dunn, J. J.
Erie—
Diller, H. E.
Rice, Edw. T.
Gettysburg—
Parsons, L. A.
Ingram—
Armor, J. C.
Johnstown—
Appel, Moses.
Kenney, E. F.
Parkhurst, C. W.
Lancaster—
Schwarz, A.
Latrobe—
Eckfeldt, J. J.
Lebanon—
Crowell, W. J., Jr.
Weimer, E. A.
McKeesport—
Clarke, E. B.
Goodspeed, G. M.
Hensen, Emil
Moore—
Werliin, G.
Munhall—
Camp, J. M.
Hartzell, L. M.
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James, R.
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Reese, P. P.
Stevens, R. H.
Natrona—
White, R. H.
New Castle—
Samuels, Wm. P.
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Goldbaum, J. S.
Palmerton—
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Holdstein, L. S.
Parnassus—
Blough, Earl
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Fahrig, E.
Flagg, S. G., Jr.
Fraley, J. C.
Furness, R.
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Hering, C.
Hess, H.
Hicks, Edwin F.
Hildebrand, J. H.
Hitchcock, F. R. M.
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Howard, G. M.
Keith, N. S.
Kitsee, I.
Lafore, J. A.
Lavino, E. J.
Lay, J. Tracy
McConnell, J. Y.
McFarlin, J. R.

Meyer, J.
Morgan, Leonard C.
Morris, H. G.
Paul, H. N.
Perry, R. S.
Queneau, A. L.
Reed, C. J.
Rosengarten, G. D.
Russell, C. J.
Sadtler, S. P.
Sadtler, S. S.
Salom, P. G.
Schamberg, M.
Smith, E. F.
Smith, E. W.
Snook, H. C.
Steinmetz, J. A.
Stevens, J. F.
Taggart, W. T.
Thwing, C. B.
Weeks, C. A.
Weisenburg, Andrew
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Werliin, Godwin
White, A. J.
Wickes, C. S.
Wirt, Chas.

Pittsburgh—
Babb, Jos. E.
Bennett, B. F.
Bradley, Jas. H.
Brown, G. H.
Brown, John T., Jr.
Connell, W. H.
Crabtree, F.
Davis, S. A.
Dewey, B.
Donkin, Wm. A.
Dougherty, J. W.
Fisher, Henry W.
Flannery, Jas. J.
Gibson, C. B.
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Hartley, R. H.
Hessom, B. F., Jr.
James, J. H.
Kemery, P.
Kier, S. M.
Laughlin, H. H.
Lincoln. P. M.
Lyon, D. A.
McDonald, R. A.
McKinley, Jos.
McKirdy, John E.
Merrill, J. L.
Mueller, H. N.
Murphy, D. H.
Ober, J. E.
Orr, R. S.
Osborne, L. A.
Page, G. S.
Pinkerton, A.
Pope, Chas. E.
Rys, C. F. W.
Rodman, H.
Sargent. G. W.
Schluederberg, C. G.
Sill, H. F.
Slocum, Chas. V.
Slocum, F. L.
Snelling W. O.
Speller, F. N.
Stewart, R. T.
Uhlenhaut, F., Jr.
Vogt, C. C.
Webb, Z.
Wiley. B.
Yardley, J. L.

Pottstown—
Cook, E. B.

Primos—
Boericke, G.
Stein, W. M.

Reading—
Merzbacher, Aaron
Parker, Jas. H.

Roaring Springs—
McDonald, F.

Scranton—
Bryden, C. L.

Sewickley—
Wadsworth, F. L.

Sharon—
Kranz, W. G.
Warren, G. S.

South Bethlehem—
Adams, L. W.
Buck, C. A.
Franklin, W. S.
MacNutt, B.
Richards, J. W.
Roush, G. A.
Seyfert, S. S.

State College—
Pond, G. G.
Taylor, F. D.
Turnock, L. C.
Walter, C. A.

Steelton—
Calder, A. R.
Carney, F. D.
Koch, S. B.
Lindemuth, L. B.
Reed, J. C.

Swarthmore—
Alleman, G.

Tarentum—
Connell, H. R.
Hitchcock, H. K.

Treichlers—
Lentz, H. N.

Tyrone—
Bachert. A. E.

West Pittsburgh—
Buch, N. W.

Wilkinsburg—
Skinner, Chas. E.

York—
Schleeder, L. B.

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Perry, C. M.

Newport—
Richards, E.

Providence—
Catlin, C. A.
Saunders, W. M.

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Mills, J. E.

Sumter—
VanDeventer, H. R.

TENNESSEE.

Chattanooga—
Thomas, B. F.

Clarksville—
Faust, T. B.

Memphis—
Holtzendorff,, P. W.

Nashville—
Cooper, K. F.
Dudley, W. L.
Washburn, F. S.

TEXAS.

Austin—
Harper, H. W.
Schoch, E. P.
Port Arthur—
Slater, W. A.

UTAH.

Provo City—
Smith, F. W.
Salt Lake City—
Bradford, R. H.
Emery, W. L.
Jennings, E. P.
Merrill, J. F.
Stalmann, Otto

VIRGINIA.

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Weaver, W. D.
Davis—
Tilley, F. W.
Holcomb's Rock—
Lee, H. R.
von Kugelgen, F.
Norfolk—
Webb, L. W.
Roanoke—
Engle, H. M.
University—
Dunnington, F. P.

WASHINGTON.

Seattle—
Crim, L. P.
Spokane—
Armstrong, L. K.
Woodwell, A. H.
Tacoma—
Everette, W. E.

WEST VIRGINIA.

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Chorpening, G. B.
Glen Ferris—
Huffard, J. B.
Morgantown—
Hite, B. H.
Wheeling—
Hearne, D. G.

WISCONSIN.

Eau Claire—
Peirce, A. E.
Madison—
Bennett, E.
Burgess, C. F.
Burling, B. B.
Hambuechen, C.
Kahlenberg, L.
Kowalke, O. L.
Richardson, L. T.
Schulte, W. B.
Storey, O. W.
Watts, O. P.
Marinette—
Lathrop, L. H.
Milwaukee—
Kremers, J. G.
Raeth, F. C.
Vogel, G. C.
Woodbury, F. E.
Zimmermann, J. G.
Wauwatosa—
Tifft, G. L.

WYOMING.

Thermopolis—
Freeman, G. N.

CANADA.

BRITISH COLUMBIA.

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Keffer, F.
Heriot Bay—
Bagot, C. G.
Nelson—
Fowler, S. S.
Vancouver—
Barwick, W. S.
Boesch, J. E.
Chappell, W. C.
Hayward, R. F.
Kendall, G. R.

MANITOBA.

Winnipeg—
Armes, H. P.
Morden, G. W.

NOVA SCOTIA.

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Cantley, T.
Sydney—
Collens, F. L.
Hitt, S. E.
Scott, A. P.

ONTARIO.

Bellville—
Evans, J. W.
Copper Cliff—
Browne, D. H.
Fitzroy Harbor—
Simpson, L.
Kingston—
Goodwin, W. L.
Guttman, L. F.
Kalmus, H. T.
Port Arthur—
Hille, F.
St. Catharines—
Heitmann, E.
Toronto—
Bain, J. W.
Burt-Gerrans, J. T.
Cohoe, W. P.
Guess, G. A.
Irving, T. C., Jr.
Kaemmerer, J. A.
Kirkegaard, P.
Loudon, T. R.
Miller, W. L.
Moffat, J. W.
Patch, N. K. B.
Tate, Alfred O.
Watts, Geo. W.
Wurster, O. H.
Welland—
Turnbull, R.

QUEBEC.

Buckingham—
Hambly, F. J.

Montreal—
Hough, A.
Jacobs, F. A.
McIntosh, D.
Pascoe, C. F.
Stansfield, A.

Ottawa—
Haanel, E.
Haff, M.
Smart, R. S.

Quebec—
McKee, J. M.

Shawinigan Falls—
Falter, P. H.
Witherspoon, R. A.

SASKATCHEWAN.

Soskatoon—
MacLaurin, R. D.

Watrous—
Smithrim, E. R.

MEXICO

Aguascalientes—
Wilkins, E. M.

El Oro—
Beignet, R.

Guadalajara—
Vrooman, H. H.

Mexico City—
Brindley, Geo. F.
Ferguson, W. A.

Pachuca—
Girdwood, K. A.

Parral—
Bradley, D. H.

Santa Rosalia—
Hobble A. C.

Teguisguiapan—
Honey, W.

Torreon—
Mills, H. P.

CENTRAL AMERICA AND WEST INDIES.

COSTA RICA.

Puntaremus—
Fraser, Lee

PANAMA.

Culebra—
Schildhauer, E.

CUBA.

Isle of Pines—
Roberts, I. L.

Jovellanos—
Weber, E. G.

Santiago de Cuba—
Bruns, C. L., Jr.

SANTO DOMINGO.

Barahona—
Monrath, Gustave

SOUTH AMERICA.

ARGENTINE REPUBLIC.

Buenos Aires—
Newbery, Jorge
Stone, J. P.

BOLIVIA.

La Paz—
Inslee, Joseph A.

BRAZIL.

Rio de Janeiro—
De Medeiros, T. S. V.
Guinle, Eduardo

S. Paulo—
De Souza, E.
Walmsley, W. N.

Villa Nova de Lima—
Davies, J. E.
Gill, T. P.
Hill, Stafford
Jones, H.

CHILI.

Antofagasta—
Atwood, C. E.

Rancagua—
Fleming, E. P.

Santiago—
Blanquier, J. T.
Diaz-Ossa, B.

COLOMBIA.

Bogota—
Calvo, P. P.

Tuquerres—
Gamba, F. P.

PERU.

Lima—
D'Ornellas, T. V.

HAWAII

Honolulu—Castle, S. N.

AUSTRALASIA.

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Gepp, H. W.

Carrington—
Lawson, J. L.

Port Kembla—
Johns M. J.
Magnus, B.
White, E. A.

Moonta Mines—
Hancock, H. L.

Sydney—
Corin, W.
Julius, G. A.

Waratah—
Schroeder, H.

NEW ZEALAND.

Dunedin—
Stark, E. E.

Epsom—
Gordon, H. A.

Wellington—
Fahy, J. T.

QUEENSLAND.

Brisbane—
Jackson, A. G.

Mt. Morgan—
Du Faur, J. B.
Richard, G. A.

SOUTH AUSTRALIA

Wallaroo Mines—
Gentles, W. C.

TASMANIA.

Hobart—
Creagh, E. C.

Queenstown—
Sticht, R. C.

AFRICA.

CAPE COLONY.

Somerset, West—Quinan, K. B.

ASIA.

CHINA.

Pekin—
Wen, C. Y.

Shanghai—
Richardson, H. K.

Tientsin—
Kwang, K. Y.

INDIA.

Bangalore—
Arunachela, T. K.

Rejouli—
Dickson, A. A. C.

Kankanhalli—
Tate, J. V. E.

JAPAN.

Akitaken—
Kawamura, T.

Kure—
Tada, S.

Kyoto—
Namba, M.
Yoshikawa, K.

Naganoken—
Takahashi, T.

Nikko—
Hasegawa, T.

Osaka—
Murahashi, S.
Nishikawa, K.

Takata—
Kunitomo, S.

Tokyo—
Hoshina, T.
Iwai, K.
Katsura, B.
Kishi, K.
Masujima, B.
Nohara, T.
Oshima, Y.

Yonezawa—
Yamasaki, J.

PHILIPPINE ISLANDS.

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Dalburg, F. A.

EUROPE.

AUSTRIA-HUNGARY.

Treibach—
Fattinger, F.

Prague—
Babrowsky, G.

Vienna—
Helfenstein, A.
Paweck, H.

BELGIUM.

Antwerp—
McBerty, F. R.
Stoll, C. G.

Brussels—
Cito, C. C.
Moltkehansen, I. J.
Solvay, A.

Vilvorde—
Olsen, H.

FINLAND.

Helsingfors—
Oholm, L. W.

FRANCE.

Livet—
Bourdon, P.

Paris—
Drake, F. E.
Gall, H.
Garfield, A. S.
Gin, G.
Keller, C. A.
Marie, C.
Ostheimer, J. W.
Riva-Berni, A.
Sang, A.

GERMANY.

Aachen—
Classen, A.

Berlin—
Glenck, I.
Reichel, W.

Bonn—
Bucherer, A. H.

Charlottenburg—
Engelhardt, V.
Fels, B.

Clausthal—
Hoffman, R.

Dresden—
Schrey, A.

Essen-Ruhr—
Goldschmidt, H.

Frankfurt—
De Neufville, R.
Liebmann, L.

Hamburg—
Arnemann, P.
Weber, E. G.
Wohlwill, H.

Hanau—
Heraeus, H.

Hanover—
Arnemann, C.

Herkrade—
Mueller, A.

Hoechst—
Reisenegger, H.

Hohenlohehuette—
Gelbach, E.

Karlsruhe—
Askenasy, P.
Haber, F.

Leipzig—
Le Blanc, M.
Schall, C.
Wagner, J.

Linz—
Calberla, R.

Lubeck—
Draeger, A. B.

Werdingen—
Meyer, F.

GREAT BRITAIN.

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Smith, C. A.
Threlfall, R.

Cardiff, (Wales)—
Ewing, A. J.

Irvine, (Scotland)—
Walker, J. W.

Liverpool—
Smith, A. T.

London—
Acheson, E. G. Jr.
Ashcroft, E. A.
Brewer, P. J.
Campbell, D. F.
Chalas, A.
Cowper-Coles, S.
Merz, C. H.
Orten-Boving, J.
Ruthenberg, M.
Shields, J.
Wilder, F. L.

Manchester—
Pring, J. N.

Sheffield—
Brook, G. B.
Cornthwaite, H.
Cornthwaite, S.
Fawcett, P.
Hadfield, R. A.
Hutton, R. S.
Robertson, T. D.
Rowland, T.

St. Helens—
Le Mare, E. B.

Walthamstow—
Wilder, F. L.

ITALY.

Aguila—
Dapples, A.

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Rome—
Catani, R.
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Morani, F.

Turin—
Giolitti, F.
Stassano, E.

NORWAY.

Arendal—
Collett, O.

Bergen—
Irgens, J. F.
Petersson, A
Turner, M. R.

Christiania—
Björnson, E.
Bryn, K.
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Hiorth, A.
Hiorth, F. V. L.
Johansen, G. H.
Styri, H.

Joessingfjord—
Borgen, A.
Refsaas, K.

Odda—
Giersten, S.

Ski—
Soederberg, C. W.

Stavanger—
Jacobsen, F.

Trondheim—
Tharaldsen, F.

Tyssedal—
Hartman, A.
Vadheim—
Kolkin, T. L.
Vennesla—
Chateau, P.

RUSSIA.

Kiev—
Yatsevitch, M.
St. Petersburg—
Lodyguine, A.

SPAIN.

Madrid—
Brewer, P. J.
Rio Tinto—
Shields, J.

SWEDEN.

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Ljungh, H.
Yngstrom, L.
Gullspang—
Hedlund, M.
Hoganas—
Akerberg, O. T.
Forssell, J.
Ludvika—
Groenwall, Assar
Lindblad, Axel
Stalhane, Otto
Mansbo—
Carlson, B.
Stockholm—
Appelberg, A. O.
Leffler, J. A.
Tingberg, Otto
Trollhattan—
Bergschold, I.
Cornelius, E.
Olausson, K. O. E.
Vesteras—
Edstrom, J. S.
Westervik—
Tillberg, E. W.

SWITZERLAND.

Basel—
Fichter, F.
Geneva—
Bonna, A. E.
Gandillon, A.
Guye, P. A.
Lacroix, H.
Turgi—
Landolt, H.
Zurich—
Liebmann, A. J.
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FIXATION OF NITROGEN BY ALUMINA AND CARBON.

By S. A. Tucker and Henry L. Read.

The object of this investigation was to find out whether nitrogen would combine with a heated mixture of alumina and carbon or with products arising from the heating of such a mixture, and to study the best conditions for bringing about the reaction.

It was furthermore desired to investigate the conditions under which ammonia could be obtained from the resulting nitrogenous product.

That aluminum and nitrogen form a compound under certain conditions of the nature AlN or Al_2N_2 has long been known[1]. This aluminum nitride is described as a gray amorphous powder. It is partly decomposed by water, forming ammonia, and this reaction also takes place on long standing in the air. Complete decomposition is effected by heating in alkali.

Ottokar Serpek was apparently the first to consider the possibility of applying the reaction of aluminous compounds with nitrogen to the fixation of atmospheric nitrogen. In numerous patents[2] in this country and abroad, he has covered the subject of aluminum nitride production, but without explaining much about the nature and conditions of the reaction. The chief point he makes is that a temperature of about 1800° to 2000°C. is essential, although in a more recent patent he mentions 1600° to 1800°C. as being permissible. He works on mixtures of alumina or aluminous compounds with carbon, the materials being in a pulverized condition, claiming that this is better than aluminum carbide. This is in accordance with the theory of Caro[3], that when aluminum nitride (AlN) is formed by heating aluminum carbide (Al_4C_3) with nitrogen, the reaction is due to the disso-

[1] Zeitschr. Anorg. Chem. **54**, 522-7 (Fichte).

[2] U. S. A. Patents 888044, 867615, 987408, 996032; German Patents 181991, 181992, 183702, 216746; British Patents 13579 (1906), 15996 (1909), 25141 (1911).

[3] Zeitsch. angew. Chem. **23**, 2412.

ciation of Al_4C_3 to Al and C. Caro found in general that more nitrogen combined around 1150°C. with Al_4C_3 if metallic Al was present, than with pure carbide, and that the largest yield of nitrogen came when aluminum alone was heated. Very little nitrogen was obtained with pure carbide, as at this temperature the dissociation is small.

Serpek's method of producing aluminum nitride (AlN) was from bauxite and carbon passed through a revolving inclined tube in the walls of which was an electric resistance furnace. Nitrogen was passed through the tube as producer gas, and being ignited at the end of the tube, the gas is used to preheat the charge. He observed that an acid gas such as HCl or SO_2 in small amount seemed to help the reaction along, though why this should be is not exactly clear.

In the experimental work, pure nitrogen was used, obtained in the early experiments by passing commercial nitrogen through a combustion furnace containing heated copper gauze to remove the oxygen which was present to the extent of 7.2 percent. In the later experiments, chemical nitrogen was used, prepared from NH_4Cl and $NaNO_2$. As a precaution, this too was passed over red hot copper. Thorough drying was effected by calcium chloride and concentrated sulphuric acid. These precautions were thought necessary, as oxygen would obviously have a bad effect by diluting the nitrogen, and by oxidizing the carbon in the charge; and water would absorb heat, and tend to increase the loss of carbon in the charge forming hydrocyanic acid. It was found that cyanogen formed in any case, but water increased the amount. Purified alumina was used, and the purest grade of petroleum coke, in all experiments except those on bauxite.

The product was analyzed for nitrogen by the Kjehldahl method. No attempt was made to find cyanamide, as Caro (*l. c.*) says that it is not formed, and even is prevented from forming with calcium carbide by the presence of Al_2O_3, around 1150°C., and lower. At the high temperatures, 1700° to 2000°C., cyanamide would decompose.

The bauxite used gave on analysis: SiO_2, 5.10 percent; Fe_3O_3, 1.56 percent; Al_2O_3, 53.76 percent; ignition loss, 31.07 percent; other substances (by difference) 8.50 percent. From this, the

amount of Al_2O_3 in the residue after ignition was 78.00 percent. The very large ignition loss is explained by the fact that bauxite contains a large proportion of water.

The early experiments were carried out in a wire wound electric resistance furnace. A very even temperature was maintained in all parts of the furnace as shown by a thermo-couple. The charge which consisted of Al_2O_3 plus 3C (10 gr. Al_2O_3 : 3.53 gr. C), finely ground and mixed, was placed in a small porcelain boat which was pushed into the tube of the furnace when the desired temperature was reached. One to two and a half grams were treated at a time. The nitrogen was led into the furnace by glass tubing passing through a cork closing one end of the furnace. Another cork through which the wires of the thermo couple passed closed the other end. A small opening in this latter cork permitted the escape of the gas. In this way air was practically excluded as there was always a slight pressure inside the furnace. The charge was dried at 110°C. before being introduced into the furnace.

A table of these results follows:

Run	Temperature	Time	Percent N	Remarks
No. 1	980-1010	1 hr.	1.64	Dry N
No. 2	990-1050	2 "	1.66	" "
No. 3	1000-1100	1 "	0.97	" " and considerable SO_2
No. 4	1000-1100	1 "	0.36	" ". and a little SO_2

Runs 1 and 2 were to determine the effect of time. Runs 3 and 4 show the effect of SO_2. This gas was generated from copper and concentrated sulphuric acid heated and introduced into the furnace by a capillary tube beside the tube for the N. The amount of SO_2 was judged by the rapidity with which it bubbled through a washing bottle containing concentrated H_2SO_4 and was controlled by a small clamp on one of the rubber connections of the SO_2 generator.

It was then desired to try the effect of a higher temperature. For this purpose a granular carbon furnace through which a tube passed for holding the charge was used, heated by a single phase alternating current. At first several porcelain tubes were used, imbedded in the granular carbon resistor (as shown in the sketch). These porcelain tubes were found, however, inadequate to stand the sudden changes in temperature. The difficulty

was overcome by using a graphite tube which was made with a bore of 5/8" diameter. The tube was provided with accurately fitted stoppers of graphite through which the nitrogen could be passed through metallic tubes threaded into the stoppers. The charge was contained in a graphite boat. Results were obtained as follows:

Run	Temperature	Time of Strong Heat	Percent N	Remarks
No. 5	1600-1700	40 minutes	3.10	Residue slightly sintered
No. 6	1800-1900	" "	22.84	Residue sintered
No. 7	1900-2200	" "	2.5	Residue fused to a globule

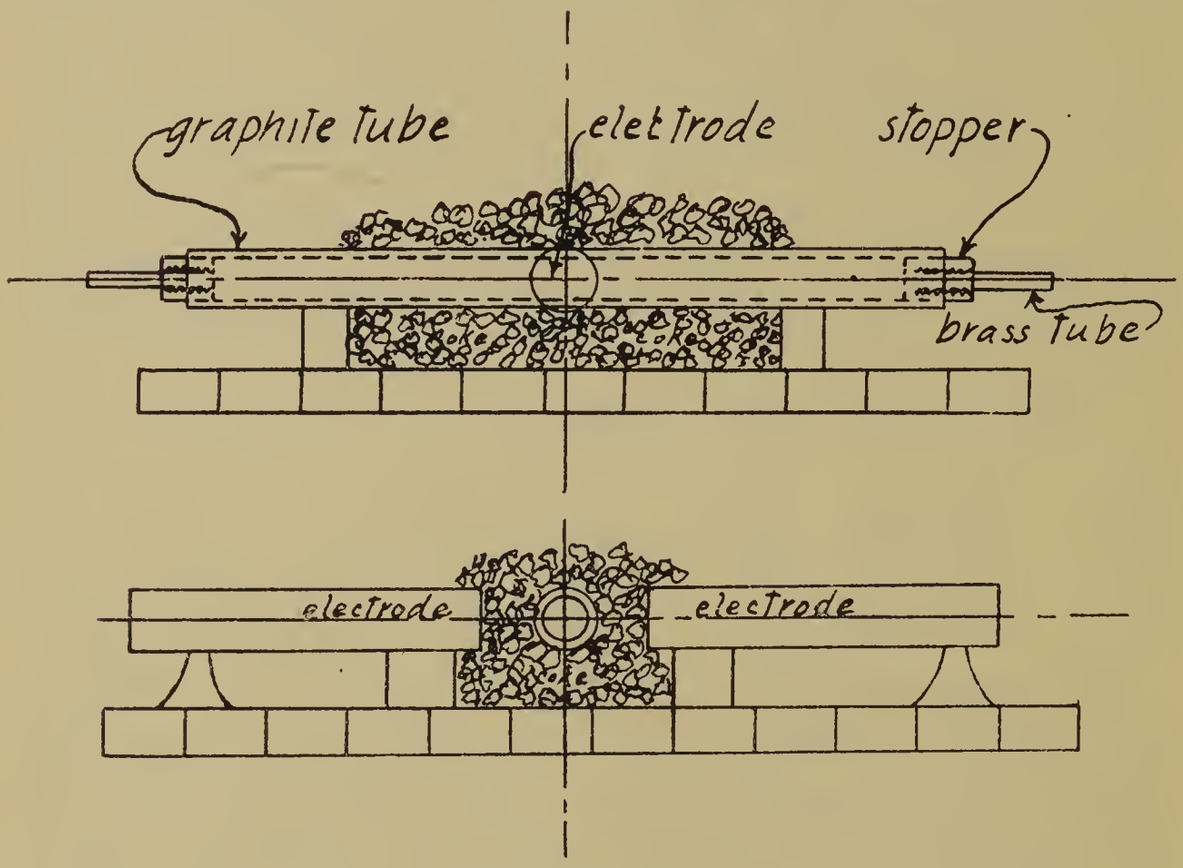


FIG. I. VERTICAL SECTIONS OF FURNACES

The amount of charge was as before about two grams each time. Some volatilization of Al_2O_3 always occurred, but no N was combined in this. The residues all had gray colors, No. 6 being fairly light. For producing the temperature in the fifth run, 30 volts and 175 amperes were used; in the sixth 33 volts and 200 amperes; and in the seventh 35 volts and 240 amperes.

The temperatures here given are estimated only, as it was impossible under the conditions to measure it accurately.

It was then desired to find out the extent of the absorption

of nitrogen in larger amounts of charge. For this purpose, a graphite crucible 3 inches high and 1¾ inches in diameter was used, accurately fitted with a graphite stopper through which was bored a hole for a hollow graphite tube extending to the bottom of the crucible. A copper tube was forced into the upper end of this graphite tube, making a tight joint, and nitrogen led to it by rubber tubing as before. The crucible was surrounded by granular carbon to protect it as much as possible from oxidation. It was placed in an upright position in the granular carbon furnace between the graphite electrodes.

The results were:

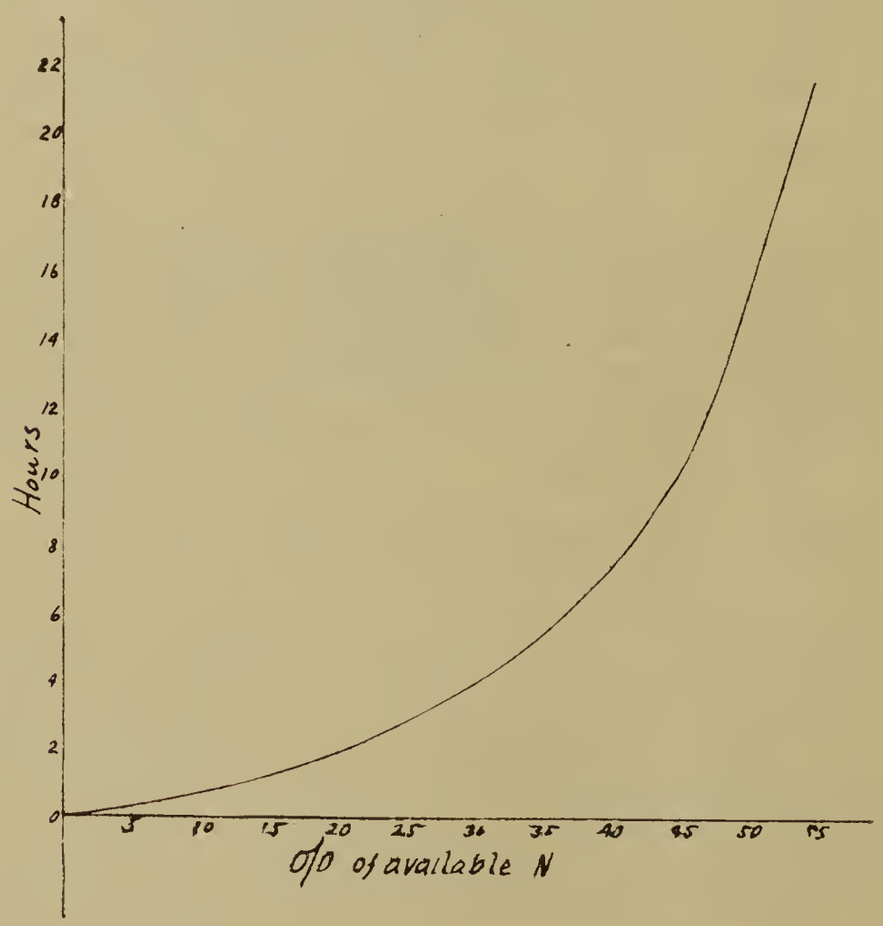
Run	Temperature	Time of Strong Heat	Average N	N in Selected Portions
No. 8	about 1900°	15 minutes	6.11%	20.46%
No. 9	" "	30 "	9.57%	30.19%
No. 10	" "	30 "	9.38%	.....

The column, "N in selected portions," is the result of the analyses of the very light gray top crust formed on top of the charge. About 20 gram charges were used. Apparently the gas formed passages for itself through the mass, and combined only on the top to any large extent. The bottom seemed very little affected. Run 10 was made with occasional stirring by a graphite rod fixed on the end of the graphite tube leading in the gas. This tube was turned around frequently. The result was that considerable graphite was rubbed off into the charge and the residue was quite black and uniform in appearance. No attempt consequently was made to find any especially rich portions. It was found possible to tell approximately when the reaction started and finished by the appearance of a flame at the vent. At times this flame gave evidences of containing cyanogen; it always contained considerable carbon monoxide. When this flame died down and disappeared, the reaction was assumed to have gone as far as it could. In the eighth run, the heating was stopped before the flame died down.

The bauxite was then mixed with carbon in the proportion to form CO from all the Al_2O_3 and SiO_2 present as well as the Fe_2O_3. It was ignited to drive off all the water after being ground to 100 mesh. The carbon was then added, and the charge put in the furnace. The results were:

Run	Temperature	Time of Strong Heat	Percent N
No. 11	about 1900-2000° C.	50 minutes	12.30
No. 12	" "	40 "	22.70

Run 11 was made in the graphite crucible. It was observed that a considerably longer time was necessary for the reaction than with pure Al_2O_3; and that some silundum was produced on the inside of the crucible. Run 12 was made in the graphite tube used in runs 5, 6 and 7, but the inside of this tube was previously given a coating of silundum by heating a charge of $SiO_2 + 2C$ to a high temperature in it. The purpose of this was to prevent graphite from being rubbed off by the charge in rotating the tube. The tube was rotated frequently to stir the charge up and allow the nitrogen to have free access to all the charge, which was kept in its place in the hottest part of the tube by two graphite plugs with small holes in them to permit the passage of the gas.



To investigate the availability of the nitrogen in the AlN prepared as described, a one gram portion was treated in a Kjeldahl flask with distilled water and boiled for a considerable length of

time. The sample was from run No. 9, containing 9.57 percent N. The results are tabulated below:

Time	Percent N	Percent of Available N
2 hrs.	1.98	20.71
5 "	3.35	35.03
6 "	3.53	36.72
7.5 "	3.84	40.13
8.5 "	4.05	42.27
9.5 "	4.19	43.82
10.9 "	4.38	45.80
11.5 "	4.46	46.61
12.5 "	4.52	47.27
13.5 "	4.60	48.02
14.5 "	4.70	49.10
15.5 "	4.78	50.00
16.5 "	4.86	50.80
17.5 "	4.93	51.58
18.5 "	5.01	52.30
19.5 "	5.08	53.12
20.5 "	5.18	54.71
21.5 "	5.24	54.76

CONCLUSIONS.

Aluminum nitride (AlN) may be formed from Al_2O_3 and C in atomic ratio 1 : 3 or 1 part by weight of Al_2O_3 to 0.353 parts by weight of C. These would be the natural theoretic proportions from the equation

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$

and they seem to be borne out by the experiments. Whenever the yield of nitrogen approached the theoretical, 34.06 percent, the product was a nearly white amorphous substance with occasional particles of undecomposed carbon.

The temperature at which the reaction is carried on is evidently of prime importance. At lower than 1600°C., the yield of combined nitrogen is trifling. Around 1800° to 2000°C., however. seems to be the right value as here was obtained the maximum amount of combined nitrogen, 30.19 percent. But it is unsafe to go above 2000° C., as shown in run 7, where decomposition of the nitride evidently took place.

The time required for the reaction is comparatively short, but it is clear that there is a limit below which the reaction is incomplete as shown by runs 8 and 9, which were carried out under exactly the same conditions except that the former was strongly heated 15 minutes and the latter 30. The nitrogen in 8 was

6.11 percent, and in 9 was 9.57 percent. When there are impurities present, a greater length of time seems necessary, as shown by the eleventh run as compared to the ninth. The question of impurities is very interesting, as little is known about their effect. SO_2 in appreciable amounts is evidently harmful. Whether in minute traces, such as would be obtained in the producer gas from a good coal, the effect might not be better than appeared in this work is, of course, an open subject, but from a theoretical standpoint there would seem to be little reason for its use. The same would apply to HCl. Producer gas as a source of nitrogen might be highly advantageous owing to its ability to burn and preheat the charge after it had been used in the reaction; and the further condition that oxygen should be absent is satisfied. Of course the CO would have the effect of diluting the N, but the harm should not be serious with a plentiful supply of gas. But impurities in the charge itself are apparently very useful, as is seen in the results on bauxite. This is probably due to catalytic action, of iron and lime particularly. It would seem that the effect of heating Al_2O_3 with C is first to produce nascent Al, which under ordinary conditions forms Al_4C_3. But in the presence of fairly pure nitrogen the aluminum seems to have a greater affinity for nitrogen than for carbon. This would appear to agree with Caro's theory that aluminum carbide heated with nitrogen forms aluminum nitride by the dissociation of the carbide, after which the aluminum attaches itself to N. This is contrary to the former opinions of some writers who hold that it was the formation of the carbide that was a necessary preliminary to the formation of the nitride. But if the above theory is correct, obviously catalytic agents would be highly desirable, and they should be substances that form nitrogen compounds without great difficulty.

Another highly important point is that the gas should have means of easily getting in contact with the charge. The N content of the top crust in runs 8 and 9, and of the whole charge in run 12, demonstrated this beyond any possible doubt. Fairly fine crushing would seem to be a necessary condition for best results. Serpek's method of bringing about this contact was by the rotating cylinder previously mentioned. He would have the difficulty of obtaining a substance for the lining of this cylinder

which could stand the high temperature and the abrasion of the charge passing over it. Carborundum might do it; so might silundum; possibly also magnesite, though it would undoubtedly wear out fairly rapidly.

As to the value of aluminum nitride as a commercial product, the ease with which ammonia can be formed is obviously the most important feature. It is well known that boiling alkaline solutions decompose it completely. Thus a source of commercial ammonia is evident, and connected with it a source of pure alumina that might well interest manufacturers of aluminum.

So far as its use as a fertilizer itself is concerned the last test described with the curve shows that it gradually evolves the nitrogen as ammonia from boiling water. If applied directly to the soil it might be expected to behave in a way not very different from this, which so far as its value as a fertilizer is concerned would be an advantage. The raw material bauxite is, however, probably too expensive to permit of its use in this manner and the nitrogen would have to be obtained as ammonia, so that the by-product alumina could be saved, either to use again in the process or in the manufacture of aluminum.

From the results of the necessarily brief set of experiments given, it is clear that, given suitable conditions, there should be no difficulty in producing a grade of aluminum nitride containing 30 percent and more nitrogen. This should give the product an advantage over calcium cyanamid which on the average runs from 17 percent to 20 percent fixed nitrogen.

Electrochemical Laboratory,
Columbia University,
May 1912.

DISCUSSION.

MR. SASSINGER:—I would like to ask a question in regard to this work. In the patents of Serpek there is made mention of the fact that a small amount of copper or other metals is used. I would like to know whether in his investigations this point was studied, whether it was necessary to add alloys in order to make nitrogen absorption more rapid.

PROF. S. A. TUCKER:—I would answer that by saying that in the patent special attention is called to various impurities which seem to aid in the reaction and particularly sulphur dioxide and hydrochloric acid. Sulphur dioxide was found to be without any advantage whatever. We did not try copper, and I am inclined to think that impurities in small amounts have a decided advantage, from the fact that you get better results using bauxite, which necessarily contains some impurities as compared with pure alumina.

PROF. JOS. W. RICHARDS:—Last month I had an opportunity of seeing this process in operation in the Savoy, and of spending a day with Mr. Serpek in Berlin, and I can confirm these statements which have been made, that bauxite itself reacts at a lower temperature than pure alumina. The bauxite of the South of France is reacted upon by nitrogen at a temperature as low as 1,550°C., and the reaction is rapid at about 1,600° to 1,700°C.; whereas pure alumina is hardly acted upon below 1,750°C. Two types of furnaces have been experimented with for the manufacture. One is a stationary furnace which is heated by a column or resistor of carbon in the center, around which the nitrogen is passed. It resembles a vertical carborundum furnace. The other is a rotary kiln, in which resistors of carbon pass transversely across, and by radiation heat the charge therein. Both those are successful in making nitride. The product, however, looks very different; that made from the vertical furnace is nearly pure aluminium nitride, sometimes in nearly colorless crystals which are unattacked by ordinary air. The product of the rotary kiln is in the form of a gray powder which contains nitrogen, but none of the crystals which are formed in the vertical furnace. I might also say that the presence of hydrogen in the gases used facilitates the reaction, which takes place at a lower temperature when hydrogen is present than when it is absent. The promoters of the process have spoken of using the alumina over and over again, but the difficulty of producing the reaction with pure alumina will probably prevent that. It probably will be more economical to start with bauxite, the impure material, and produce alumina as a by-product of the process.

A Paper read before Section Xa: Electrochemistry, VIII International Congress of Applied Chemistry, New York City, September 6, 1912.

THE ACTION OF NITROGEN ON STRONTIUM CARBIDE.

By S. A. Tucker and Y. Tsenshan Wang.

The action of nitrogen on lithium carbide has already been investigated[1]. The present work with Strontium Carbide was taken up in the same manner, and included the following:

(1) Preparation of strontium carbide and analysis of the product.

(2) Absorption of nitrogen by the carbide and the influence of time, temperature, and pressure.

(3) Analysis of the product, and conclusions.

Preparation of Strontium Carbide.

Moissan[2] obtained strontium carbide under the same conditions as the carbide of calcium, by heating a mixture of 150 parts strontium carbonate and 50 parts of sugar carbon in his horizontal arc furnace. The power used is stated at 24.5kw., using 350 amperes at 70 volts. The duration of the run was 15 minutes. The product obtained by Moissan was a blackish mass with a crystalline brown fracture, decomposing in moist air, and agreeing in its general properties with the other alkaline-earth carbides.

In the preparation of strontium carbide for this work, the same general method was employed. The furnace used was of the vertical-arc type[3], consisting of a graphite crucible about 4-in. (10 cm.) diameter which constitutes one of the electrodes, the other electrode is a vertical graphite rod. Proper heat insulation is provided and the heating can be carried on by direct arc or partially by resistance. Strontium carbonate and coke were used for the raw materials and both were selected with a view to their

[1] Tucker and Moody, Jour. Am. Chem. Soc., 33, 1478 (1911).
[2] Le Four Electrique, p. 301; Paris, 1897.
[3] Tucker, Vertical Arc Furnace, Electrochem. and Met. Eng., 4, 263 (1906).

purity. On heating to a temperature of about 2,000°C. the following reaction takes place:

$$SrCO_3 + 4C = SrC_2 + 3CO.$$

A number of runs were made to ascertain the best conditions of heating and the proportions of the charge best suited to the formation of the carbide, which proportions might differ from the theoretical. The difficulties arising in the preparation of strontium carbide are the same as are found in the formation of lithium carbide[4], and arise from the fact that its formation and decomposition temperatures lie close together, resulting in the presence of decomposition products in the resulting carbide. The tendency however is less prominent with strontium than it is with lithium, and for that reason it is much easier to prepare the carbide of strontium. The quality of the carbide was determined by evolving the acetylene from a weighed sample in a Rose and Geissler alkalimeter, by the application of cold water, as follows:

$$SrC_2 + 2H_2O = C_2H_2 + Sr(OH)_2$$

The gas was carefully dried by passing over calcium chloride, the loss in weight being equivalent to the acetylene evolved. About 150 grams of the mixture of the carbonate and coke were taken for each run for which the data are given in the following:

TABLE I.

No.	Time Minutes	Power Kw.	Carbide Content of Product Percent
1	5	2.5	72
2	6	3.2	73
3	12	3.0	72
4	15	3.0	73
5	22	3–4.2	62
6	25	3–4.2	60

Alternating current was used with about 35 volts at the arc. Nos. 5 and 6 were samples from the product of No. 3 and No. 4, heated for 10 minutes further at a slightly increased power, and shows that prolonged heating results in decomposition and consequently a lower value of the carbide content.

[4] Tucker and Moody, Jour. Am. Chem. Soc. 33, 1480 (1911).

Absorption of Nitrogen by the Carbide.

The nitrogen for this part of the work was prepared chemically, by heating a strong solution of ammonium chloride in a large flask and introducing a solution of sodium nitrite gradually by means of a stop-cock funnel tube. By regulating the supply of the nitrite in this way a brisk evolution of the gas can be maintained. After washing, the gas was stored in gasometers until required for use. The gas so prepared contains a small quantity of oxygen, and in order to remove this it is necessary to pass the gas over copper gauze heated to a low-red heat in a combustion furnace.

The nitrogen obtained by the Linde process as a by-product in the manufacture of oxygen was tried in these experiments, but was found to contain so large a content of oxygen that it required a very careful treatment with hot copper to render it fit for use. The method of carrying on the absorption of the nitrogen by the strontium carbide was to heat the carbide in an electric tube furnace[5] by which the temperature can be regulated and maintained at the desired point. The carbide was placed in a porcelain boat, situated in the tube of the electric furnace at such a position that it nearly touched the junction of the thermocouple which was used to measure the temperature.

The nitrogen from the gasometer was dried over calcium chloride before entering the heated copper gauze, and was further dried by passing through two bottles containing sulphuric acid. The dried and purified nitrogen was then admitted to the tube of the electric furnace, which was not heated until all the air had been displaced. The temperature was then raised so that the carbide was subjected to the required heating in an atmosphere of nitrogen.

In some of the experiments it was found better to introduce the carbide after the electric furnace had come to the required temperature.

In order to study the influence of pressure on the absorption, a small steel tube was used[6] which had a tight-fitting threaded plug at one end for the introduction of the sample in a small steel

[5] Tucker, Electric Furnace with Calorite Resistors for the Laboratory. Jour. Ind. and Eng. Chem., 3, 595 (1905).

[6] Tucker and Moody, Jour. Am. Chem. Soc., 33, 1483 (1911).

boat. A side tube provided means for the admission of nitrogen, which was raised to the required pressure by a force-pump operated by hand.

The steel tube itself was of such size as to fit easily in the porcelain tube of the electric furnace. Before admitting the nitrogen the air was exhausted by a Geryk oil vacuum pump.

Analysis of the Product and Conclusions.

The product obtained after treatment with the nitrogen was usually caked, the surface was white, another under portion brownish-black to gray. The total nitrogen was determined by the Kjeldahl method.

In order to ascertain in what condition the nitrogen existed in the product, the method of analysis recommended by N. Caro[7] was used. This consists in treating a sample of the product with excess of ammoniacal silver acetate solution, which precipitates silver cyanamid. The precipitate is washed free of ammonia and the nitrogen in it determined by the method of Kjeldahl. The filtrate is then treated with caustic potash, and boiled to free the ammonia. The precipitate so formed is silver dicyanamid, the nitrogen content of which is also determined by the Kjeldahl method.

For the cyanide the method of W. Feld[8] was employed, which consists in boiling the sample with a strong solution of lead nitrate. The distillate is collected in caustic potash solution and the cyanide determined by titrating with silver nitrate, using potassium iodide as indicator.

The following results were obtained:

TABLE. II.

Influence of Temperature.

No.	Temperature °C	Nitrogen Percent	Time Hours
1	500	0.437	1
2	800	1.297	1
3	1000	6.89	1
4	1000	0.76	1
5	1000	6.65	1
6	1150	8.60	1

[7] Caro, Schuck and Jacoby, Zeit. angew. Chem., 23, 2405 (1907)

[8] Feld, J. Gasbeleuchtung, p. 46.

Influence of Time.

No.	Temperature °C	Nitrogen Percent	Time Hours
7	1000	9.08	3

Influence of Pressure.

No.	Temperature °C	Pressure Lbs. Sq. Inch	Nitrogen Percent	Time Hours
8	1000	35	5.8	1
9	1000	45	5.27	1

From these results it appears that nitrogen is only absorbed by stronium carbide at fairly high temperatures, which follows from Nos. 5 and 6, and that the influence of time is important, as shown in No. 7.

Nitrogen under pressure is evidently without advantage for its absorption by this carbide.

The Condition in which the Nitrogen Exists in the Product.

Analyses were made on several samples of the product as follows:

Total nitrogen No. 7 =	9.08%
Nitrogen as cyanamid =	2.25
Nitrogen as dicyanamid =	0.36
Nitrogen as cyanide =	5.90
Total nitrogen No. 3 =	6.89%
Nitrogen as cyanamid =	3.62
Nitrogen as dicyanamid =	0.24
Nitrogen as cyanide =	2.15
Total nitrogen No. 6 =	8.60%
Nitrogen as cyanamid =	3.19
Nitrogen as dicyanamid =	trace
Nitrogen as cyanide =	1.54

These results, while not entirely satisfactory, show that some of the nitrogen is fixed by this carbide as cyanide, which is quite different from the product obtained by the absorption of nitrogen by the carbides of calcium and lithium, in which cases the main

product is cyanamid with only a trace of cyanide. We believe that the method of analysis, particularly for the determination of the cyanide, is not very accurate and that this accounts for the discrepancies, particularly in product No. 6.

In conclusion we find that strontium carbide absorbs nitrogen at atmospheric pressure when heated to a temperature of from 1,000° to 1,200°C., and that the product so formed contains an appreciable proportion of cyanide.

Electrochemical Laboratory,
Columbia University.

A Paper read before Section Xa: Electrochemistry, VIII International Congress of Applied Chemistry, New York City, September 11, 1912.

STUDY OF A SMALL CARBORUNDUM FURNACE.

By Wilder D. Bancroft, L. V. Walker and C. F. Miller.

In the runs to be described we have determined the amount of crystallized carborundum formed, but not the size of the crystals. While this last is important from the technical point of view, it lay outside the scope of this paper, which is in itself merely a preliminary one. We have studied the yields in a 30 kw. and a 20 kw. experimental furnace, as affected by length of run. A granular carbon core was used for this series of experiments; but it is hoped some day to make runs with a graphite core, working with a lower voltage and a higher current.

At first the furnaces were built of Queen's Run fire-brick, laid loosely together; but it was soon found more convenient to lay the bricks in mortar so as to prevent any possibility of the side walls breaking down during a long run. The furnace was 27 inches (68 cm.) in length, 16 inches (40 cm.) in width, and about 23 inches (58 cm) in depth. The walls were 4 inches (10 cm.) thick, the width of a brick. The lower two bricks in the side walls were staggered so as to cut down the dead space.

The runs to be described were made with graphite electrodes 2 x 4 x 24-inch (5 x 10 x 60 cm.) clamped tightly in water-cooled electrode holders designed by Mr. Gillett and made by Champaign Brothers of Ithaca. They consist of a plate 8 x 4 x ⅞-inch (20 x 10 x 0.9 cm.) to which is attached a box four inches square and two inches deep. Through the cover of this box there pass two tubes each of ¼-inch (0.6 cm.) bore. One tube passes just through the cover and the other nearly to the bottom of the box, water being let in through the second pipe and out through the first. The electrode holders are made of cast-bronze, and when two are clamped on opposite sides of an electrode, there is a possibility of 32 square inches (200 sq. cm.) of cooling surface.

By putting a thermometer at the inlet tube and another at the outlet tube it is easy to determine radiation losses, provided one weighs the water which has passed through the electrode holders. With a moderate volume of water flowing, the electrodes can be kept fairly cool even with a current of 1000 amperes or more. In the first run we made the mistake of bolting the electrode holders to the electrodes some little distance from the furnace walls, with the result that a marked disintegration of the electrodes took place. In the next run the electrode holders were shoved close against the furnace walls.

The electrodes passed through the end walls of the furnace, at a point central to the cross-section of the charged furnace, and extended a distance of 5.5 inches (14 cm.) with the furnace walls, making direct contact with a 4 pound (18 kg.) granular carbon core, two inches (5 cm.) wide, four inches (10 cm.) deep, and 16 inches (40 cm.) long.

The materials used in the charge were as follows:

Sand: White sand supplied by the Carborundum Co.

Analysis: 99.4 percent SiO_2, 0.4 percent residue HF treatment, 0.2 percent loss on ignition.

Coke: Supplied ground to 14 mesh (6 per cm.) by the Acheson Graphite Co.

Analysis: 10 percent ash, 3 percent moisture, 83 percent total carbon, 4 percent volatile.

Sawdust:

Analysis: 38 percent carbon.

Commercial Salt.

The normal charge was: sand 53.5 percent, coke, 40 percent, sawdust, 5 percent, and salt, 1.5 percent; 190-200 lb. (86-91 kg.) being used in each run. This composition corresponds to a 10 percent excess of carbon over that calculated from the equation,

$$SiO_2 + 3C = SiC + 2CO.$$

It has been found by experiment that the 10 percent excess of carbon is required to prevent the formation of silicon carbide within the core. If the coke used in the charge were all available

and were neither so fine as to be removed by escaping CO nor so large as to become silicon-coated instead of being converted into carborundum, this excess would not be necessary.

The power available in the electrochemical laboratory consists of a G. E. motor-generator, form K, type 1, 60-cycle, 2200-volt 150-h. p. induction motor, with starting compensator; the motor is directly coupled to a form A, class 6, 2000-ampere, 35-volt, 27.4-cycle, 75-h. p., double-current generator, from which alternating current is drawn through a form B-1, type OO, 150-h. p. oil-transformer. The generator is separately excited by a form H, class 2, 125-volt, 26-ampere D. C. generator. With such an apparatus, by suitable adjustment of the transformer ratios, any voltage from 25 to 200 was obtainable in steps of about 1 volt. The voltage across the furnace was read on a Thomson double-scale voltmeter, and the current on a 2100-ampere Leeds and Northrup mercury ammeter. Owing to an accident to the ammeter, a few of the runs were made using a current transformer having a ratio of 1 : 45.5, connected in series with the furnace, and the current calculated from observations on a 30-ampere Thomson instrument.

In every experiment the normal charge was weighed out to total 200 lb. (91 kg.) and intimately mixed. It was then placed in the furnace even with the bottom of the electrodes. Two pieces of sheet-iron were then placed on each side of the electrodes, thus forming a rectangular cavity in which to place the crushed carbon core. The sheet-iron can be held in place by packing some of the charge against the outer sides. It is very important to pack that part of the charge in which the core rests, as even at best there is sure to be a considerable settling of the core as the run proceeds, which will alter the core shape. It is interesting to note here that were other shapes of core desirable a very convenient method for working would be to use paper forms, as the paper will soon burn off and introduces no new variables. The rest of the charge was then added; sheet-iron plates carefully removed so as not to alter the core shape, and then the charge built up so as to conform to the outer surface of a watermelon, it being observed after the first run that the heat radiation follows such a curve.

In practically all the efficiency runs, in order to check the conditions as closely as possible, temperatures were read at the core, using all three high-temperature instruments at hand, the Thwing, Wanner, and Morse, which are fully described in Dr. Gillett's paper on high-temperature measurements.[1] This was made possible by the use of Gillett's temperature tube for use in carborundum furnaces, which is also fully described in the above article. It was found that a brass tube, inserted in the end of the carbon tube and attached at the other end to a flexible metal tube, gave greater satisfaction than the glass-rubber connection used by Gillett, there being less chance of fracture in handling the suction tubes, from which silica deposits must be removed at intervals in order to keep the tubes from clogging. When building the furnace a Gillett tube was placed so that the graphite plug rested directly against the core, midway between the two electrodes, the tube being supported by the charge and also, at the suction end, by a hole drilled in the brick wall through which the tube extended for about half an inch. The composition of the tube changes with the run, being partially converted into carborundum. In order to keep the results strictly comparable a new tube was made for each run.

As an interesting check on the rate of heating a Pt: Pt-Rh thermocouple was placed 8 inches (20 cm) to the left of the Gillett temperature tube and 4.5 inches (12 cm.) from the core. Readings were taken every 5-10 minutes throughout the run. The data are given in Table I.

[1] Jour. Phys. Chem. **15**, 213 (1911).

TABLE I.

30 Kw. Run, 8 Hours.

Time	Amperes	Volts	Core Temperature °C	Thermo-couple °C	Kw. Observed
10.00	10	160			1.6
.05	50	160			8.0
.10	25	160	1250	20	3.5
.15	200	160	1360		32.0
.20	310	92			28.5
.25	325	72	1760		23.4
.30	400	78	2240		31.2
.35	475	72	2250	20	34.2
.40	500	64		40	32.0
.45	510	59	2400	50	30.1
.50	530	56	2400	60	29.7
.55	550	54		60	29.7
11.00	560	53	2420	60	29.7
.05	570	52		70	29.7
.10	590	50	2460	75	29.5
.15	600	50		90	30.0
.20	605	49	2490	100	29.6
.30	635	47		150	29.8
.35	660	47	2490	185	31.0
.40	640	45		225	28.8
.45	630	45		260	28.4
.50	640	44	2520	315	28.2
.55	670	45		330	30.1
12.00	680	44	2550	385	29.9
.05	680	44		430	29.9
.10	695	43		475	29.9
.15	690	42	2550	550	29.0
.20	690	42		590	29.0
.25	705	43		620	30.3
.30	735	43			31.6
.40	710	41	2550	745	29.1
.45	735	42		790	30.9
.50	740	42			31.1
.55	720	40		880	28.8
1.00	725	41	2550	895	29.7
.05	720	41			29.5
.10	740	41		965	30.3
.15	740	40	2520	1010	29.6
.20	740	40		1035	29.6
.25	735	40		1065	29.4
.30	750	40		1090	30.0
.35	760	40	2500	1130	30.4
.40	770	40		1150	30.8
.45	765	40			30.6
.50	765	40		1195	30.6
.55	775	40	2460	1225	31.0
2.00	770	40	(fumes)	1250	30.8
.05	775	40		1270	31.0
.10	760	39	2350	1300	29.6
.15	770	39	(fumes)		30.0
.20	760	39		1335	29.6

TABLE I—*Continued.*

Time	Amperes	Volts	Core Temperature °C	Thermo-couple °C	Kw. Observed
.25	770	39		1360	30.0
.30	770	39		1380	30.0
.35	765	39	2500	1390	29.8
.40	760	39		1400	29.6
.45	760	39		Limit of	29.6
.50	755	39	2500	Pt-Rh ther-	29.4
.55	760	39		mo-couple	29.6
3.00	760	39			29.6
.05	775	40	2480		31.0
.10	780	40	(Small		31.2
.15	760	39	carbon		29.6
.20	760	39	tube		29.6
.25	760	39	burned		29.6
.30	760	40	out)		30.4
.35	760	40			30.4
.40	760	40			30.4
.50	775	40			31.0
.55	755	40			30.2
4.00	760	40			30.4
.05	750	40			30.0
.10	740	39			28.9
.15	740	40			29.6
.20	750	40			30.0
.25	760	40			30.4
.30	760	40			30.4
.35	760	40			30.4
.40	760	40			30.4
.45	765	40			30.6
.50	760	40			30.4
.55	755	40			30.2
5.00	755	40			30.2
.05	760	40			30.6
.10	750	40			30.0
.15	780	41			32.0
.20	750	40			30.0
.25	750	40			30.0
.30	740	40			29.6
.35	735	40			29.4
.40	735	40			29.4
.45	735	40			29.4
.50	720	40			28.8
.55	750	40			30.0
6.00	740	40			29.6

Summary.

Core	3.75	lbs.	(1.7 kg.)
Charge	198	"	(90 ")

Yield.

Siloxicon	72.0	lbs.	(33 kg.)
Unchanged Charge	61.0	"	(28 ")
Graphite	3.5	"	(1.6 ")
SiC	12.75	"	(5.8 ")

Table II.

30 Kw. Run, 8 Hours.

Average Kw. Observed	Kw. Hours	Calculation of Kw.-hour Input			
		Average Kw. Observed	Kw Hours	Average Kw. Observed	Kw. Hours
4.8	0.40	30.6	2.55	31.0	2.58
5.8	0.48	30.7	2.56	31.0	2.58
15.8	1.32	30.6	2.55	30.0	2.50
30.2	2.52	30.8	2.57	29.8	2.48
26.0	2.16	30.9	2.57	29.5	2.46
27.3	2.28	30.9	2.57	29.4	2.45
32.7	2.72	29.8	2.48	29.4	2.45
33.1	2.76	29.8	2.48	29.1	2.42
31.1	2.59	29.8	2.48	29.4	2.45
29.9	2.49	29.8	2.48	29.8	2.48
29.7	2.47	30.0	2.50		
29.7	2.47	29.9	2.49	Total	234.36
29.7	2.47	29.7	2.47		
29.6	2.46	29.6	2.46	Kw. hrs. input Carborundum 24.7g Kw. hrs.	
29.8	2.48	29.5	2.46		
29.8	2.48	29.5	2.46		
29.7	2.47	29.6	2.48		
29.7	2.47	29.8	2.48		
30.4	2.53	31.1	2.59		
29.9	2.49	29.9	2.49		
28.6	2.38	29.6	2.46		
28.3	2.36	29.6	2.46		
29.1	2.42	30.0	2.50		
30.0	2.50	30.4	2.53		
29.9	2.49	30.4	2.53		
29.9	2.49	30.4	2.53		
29.5	2.46	30.7	2.56		
29.0	2.42	30.6	2.55		
29.6	2.46	30.3	2.52		
31.0	2.58	30.2	2.52		
31.0	2.58	29.5	2.46		
29.8	2.48	30.0	2.50		
30.0	2.50	29.8	2.48		
31.0	2.58	30.2	2.52		
29.9	2.49	30.4	2.53		
29.2	2.43	30.4	2.53		
29.6	2.46	30.4	2.53		
29.9	2.49	30.5	2.54		
29.9	2.49	30.5	2.54		
29.6	2.46	30.3	2.52		
29.5	2.46	30.2	2.52		
29.7	2.47	30.4	2.53		
30.2	2.52	30.3	2.52		

Owing to the fact that accurate wattmeters are not made which are adjustable to widely varying currents and voltages, and since it seemed inadvisable to purchase apparatus that could perhaps be used for only the one research, no corrections have been made for power factor, and all that we have calculated as input is 'observed' kilowatt hours. The average 'observed' kilowatts were taken for a given interval and were calculated to kilowatt hours. The sum of all these observations gives the total kilowatt hours input for the run. Dividing the grams of carborundum formed by the input gives mean grams of carborundum formed per kilowatt hour. The data are given in Table II.

One of the pleasant things about this research was that absolutely no difficulty was experienced in separating the products of the run. Consequently it is reasonable to claim a fair amount of accuracy in recording yields. The furnace is usually cool enough to dismantle 36-48 hours after the run is over. The first coat to be removed is a thin crust of fused sand covering the charge, which is always rigid enough to be skimmed off readily with the hand. The unchanged charge is next in order and, being powdery, has to be removed with a spoon. By forcing a scoop-shaped pan under the siloxicon layer, which presents a greenish-gray appearance, and then extracting the electrodes carefully, siloxicon, carborundum, graphite, and core can be removed together and will remain intact. Some of the core, however, becomes graphitized, so that the core settles a great deal, leaving an open space between the upper formation of crystallized graphite and the core. When the stationary stage has been reached in the furnace, a cross-section through the center of the furnace perpendicular to the core shows concentric cylinders of graphite, carborundum and siloxicon whose wall thicknesses are 2 inches and 3 inches (5-7.5 cm.) respectively. This wall thickness falls off gradually towards the end walls of the furnace, which indicates very clearly the heat gradient throughout the furnace. The carborundum layer is the most rigid, so that the siloxicon can be easily separated from it by hand, the line of demarcation being the point where the sharp SiC crystals prick the hand. The graphite is removed from the other side of the carborundum layer by brushing with a test-tube brush, and whatever

graphite remains with the core can be sifted out through a 14-mesh (6 per cm.) sieve. This method of separation proved sufficiently accurate, in that runs could be duplicated almost exactly, the yields never varying more than an ounce or two. A summary of the results is given in Table III.

TABLE III.

Summary of Efficiency Runs—30 Kw. Series.

No.	Time of Run Hours	Charge		Core		Graphite		Siloxicon		SiC		Grams SiC per Kw.-hr.
		Lb.	Kg.	Lb.	Kg.	Lb.	Kg.	Lb.	Kg.	Lb.	Kg.	
1	2.0	180	82	4	2	0.75	0.34	16.75	7.6	5.00	2.3	40.2
2	2.5	190	86	4	2	0.75	0.34	17.00	7.7	7.50	3.4	47.5
3	3.0	195	89	4	2	1.00	0.42	24.50	11.1	8.00	3.6	47.1
4	3.5	190	86	4	2	1.37	0.62	27.00	12.3	9.00	4.1	44.5
5	4.0	193	88	4	2	1.50	0.68	30.00	13.6	10.00	4.5	42.5
6	4.5	197	90	4	2	2.37	1.08	34.50	15.7	11.00	5.0	39.2
7	6.0	198	90	4	2	3.25	1.48	51.00	24.1	12.75	5.8	31.8
8	8.0	198	90	4	2	3.50	1.38	72.00	32.7	12.75	5.8	24.7

20 Kw. Series.

1	2.5	200	91	4	2	0.62	0.28	13.00	5.9	2.75	1.3	25.3
2	3.5	200	91	4	2	0.87	0.40	19.00	8.6	3.87	1.8	25.4
3	6.0	200	91	4	2	1.87	0.85	26.50	12.0	7.87	3.6	29.0
4	10.0	200	91	4	2	3.25	1.48	47.00	21.4	12.75	5.8	23.5
5	14.0	199	90	4	2	3.75	1.70	72.00	32.7	10.25	4.7	16.3

From the data for the two series of runs, together with that for the 30 kw. 8-hour run taken as a typical experiment, curves have been plotted to show the furnace regulation, variation in temperatures at the core and at the surface of the furnace with the time, the rate of increase in the total yield, and the yield in grams per kw.-hr. for different periods of run.

In a typical run the potential drop across the furnace is raised rapidly to about 160 volts and is held there until the furnace is brought up to load and is then lowered as much as is necessary to keep the heating rate constant at the desired value. In about half an hour the voltage can usually be dropped to 50 volts and from then on there is a gradual drop in potential corresponding to a similarly gradual increase in the current. Hence in a very

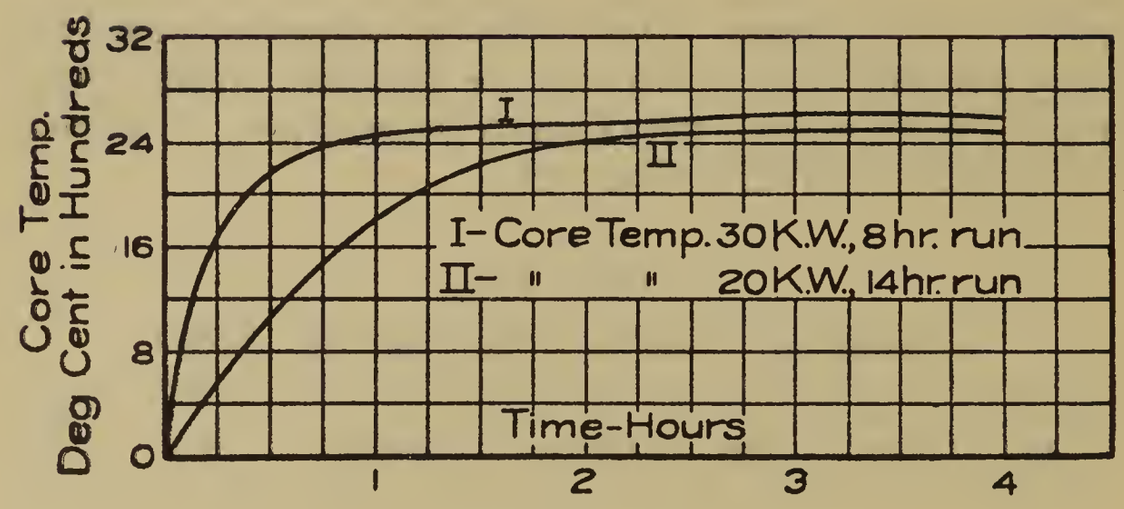

Core Temp.
Deg Cent in Hundreds
32
24
16
8
0
I
II
I- Core Temp. 30 K.W., 8 hr. run
II- " " 20 K.W., 14 hr. run
Time-Hours
1
2
3
4

FIG. 1.

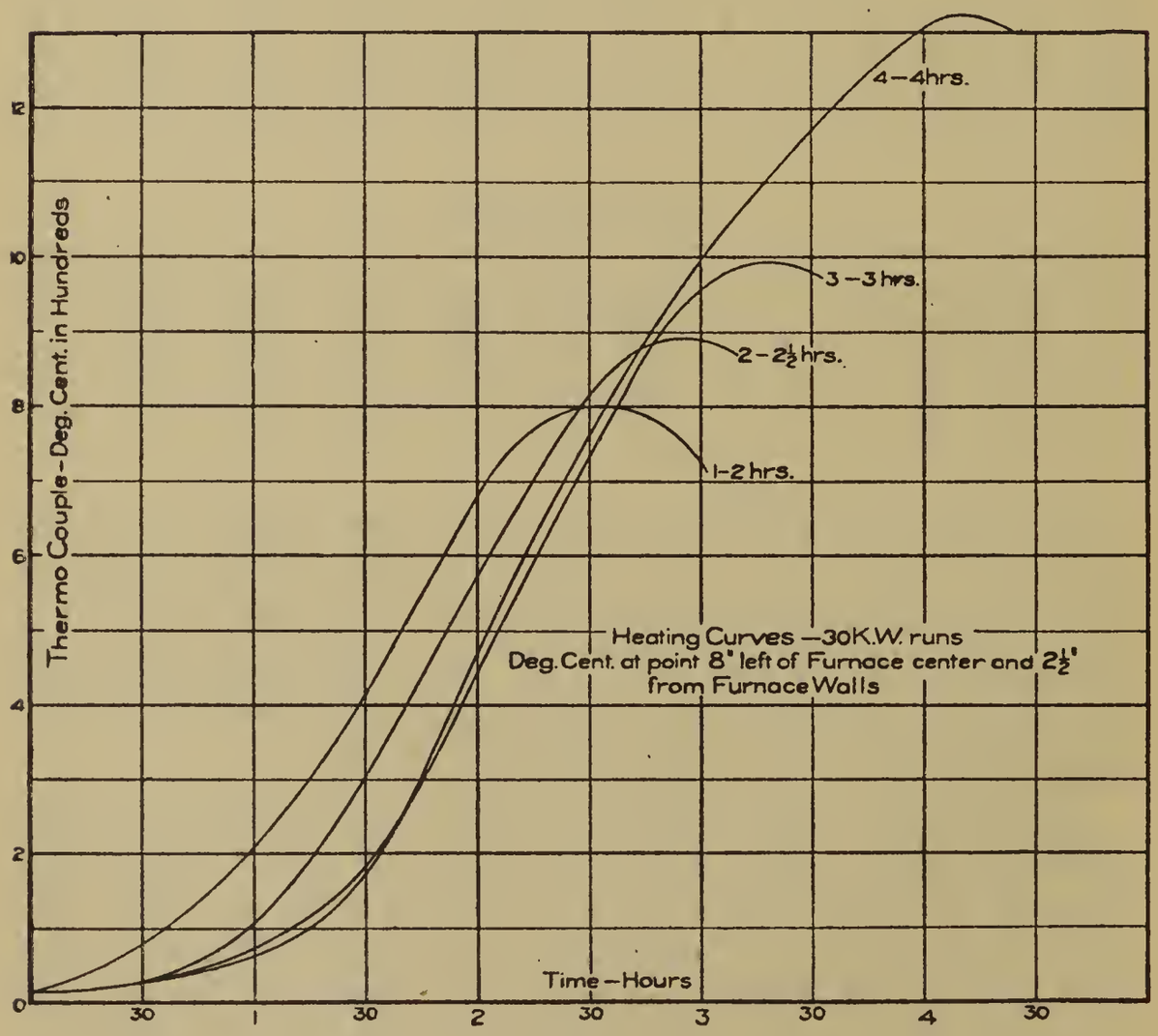

Thermo Couple - Deg. Cent. in Hundreds
0
2
4
6
8
10
12
4 - 4 hrs.
3 - 3 hrs.
2 - 2½ hrs.
1 - 2 hrs.
Heating Curves - 30 K.W. runs
Deg. Cent. at point 8" left of Furnace center and 2½"
from Furnace Walls
Time - Hours
30
1
30
2
30
3
30
4
30

FIG. 2.

short time from the start the furnace regulation becomes a simple matter. This is in agreement with the curve, Fig. 1, showing the core temperatures at different intervals throughout the run. The rise in core temperature is very rapid during the first 30-60 minutes, and from then on the temperature remains nearly constant. To show that the rate of heating in different runs approximates similar conditions, there are given in Fig. 2 curves showing the rise in temperature at a point 8 inches (20 cm.) to the left of the core center and 4.5 inches (12 cm.) from the core. A very gradual even rise in temperature is characteristic of these curves.

We now come to a consideration of yields. In Fig 3 are the yields in pounds of carborundum, siloxicon, and graphite for the 30 kw. furnace, while the corresponding results for the 20 kw. furnace are given in Fig 4. The formation of graphite appears to follow approximately a straight line curve for some time, and then starts to bend at about the time that the carborundum formation has reached its limit. The siloxicon curves show a slight bend in the opposite direction at this same point. It is almost self-evident that this would be the case, owing to the fact that the carborundum layer has arrived at a maximum radiation surface as well as at a maximum temperature, and hence is most efficient in heating the siloxicon and unchanged charge about it. The slight decrease in the rate of formation of graphite is hard to explain except by the stationary-stage theory, as there is always a layer of carborundum which could furnish carbon on decomposing, also an excess of carbon in the core itself. It may be that the carbon in the core is not as available owing to the size of the granules. This bend might also be explained as experimental error were there not a striking resemblance in the graphite curve both of the 20 kw. and of the 30 kw. furnace.

As was anticipated from the beginning, the carborundum curves show a flat, indicating that at this point the heat given off by the SiC is equal to the calories received from the graphite and core, none of the energy being expended to raise the temperature of the SiC layer. This is the beginning of the stationary stage. In the 30 kw. furnace we reach such a point in 6 hours of run, Fig. 5; in the 20 kw. furnace at the end of 10 hours. The 14-hour run on

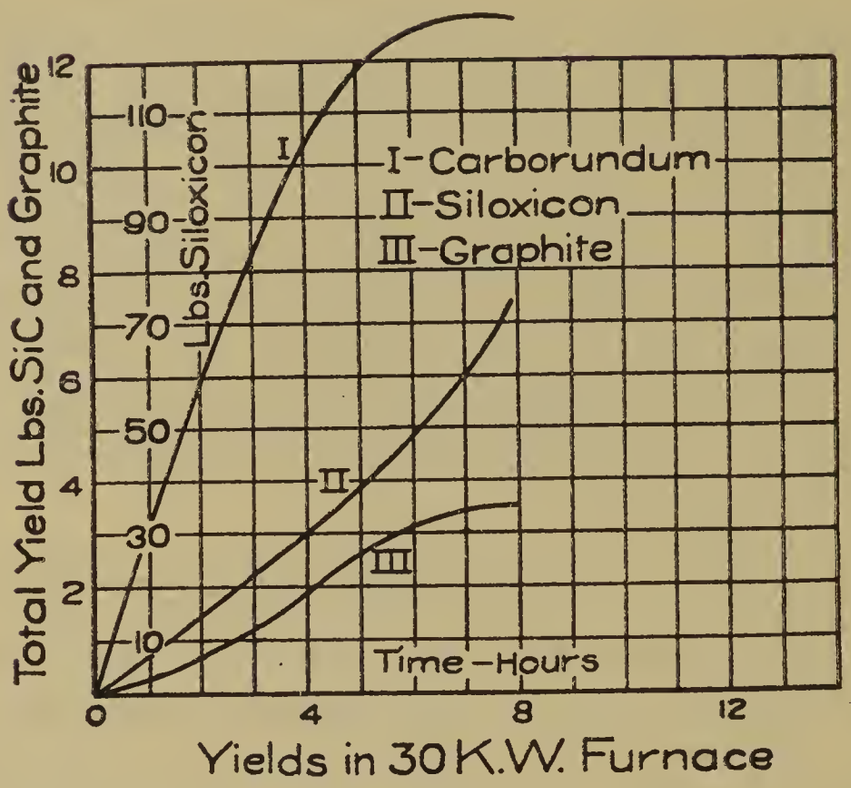

Total Yield Lbs. SiC and Graphite
Lbs. Siloxicon
I-Carborundum
II-Siloxicon
III-Graphite
Time-Hours
Yields in 30 K.W. Furnace

FIG. 3.

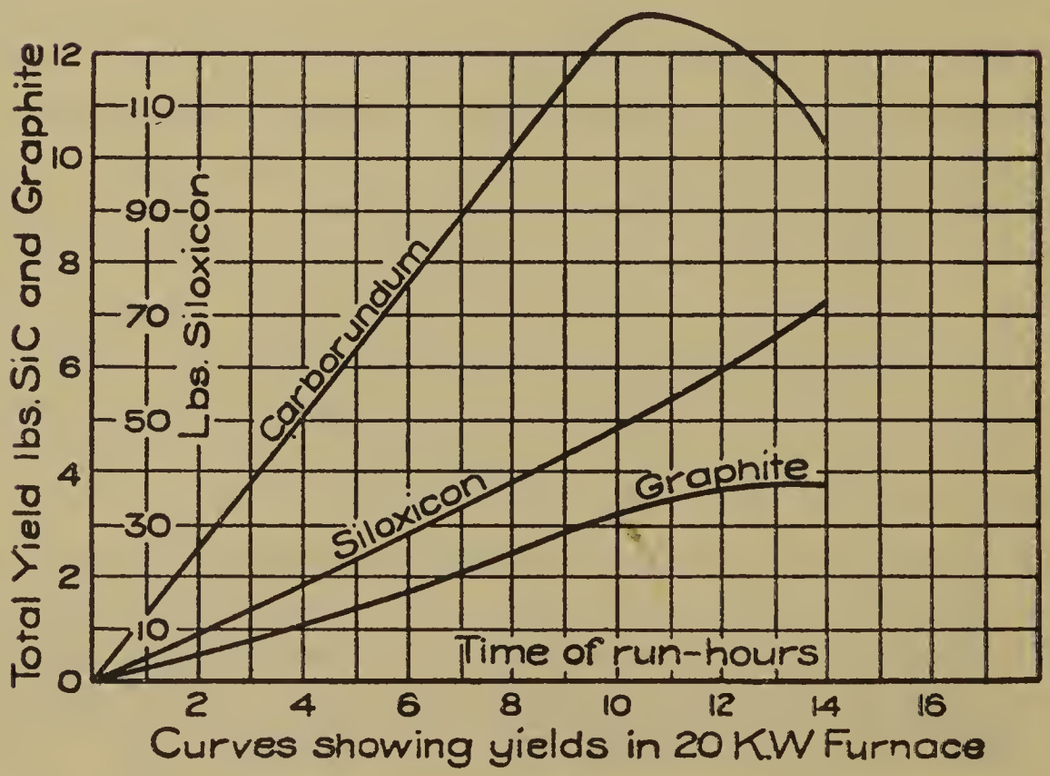

Total Yield lbs. SiC and Graphite
Lbs. Siloxicon
Carborundum
Siloxicon
Graphite
Time of run-hours
Curves showing yields in 20 K.W Furnace

FIG. 4.

the 20 kw. furnace shows that the conditions for a stationary stage are by no means permanent in the carborundum furnace, and that there is such a thing as a rapid decomposition of SiC if the run be continued too long. This could be explained as due to the high heat-insulating effect of the then rapidly increasing siloxicon yield, which would confine more heat in the SiC zone, causing the SiC to decompose at an increased rate. It is unfortunate that a 12-hour, 20 kw. run could not have been made, or else a longer run on the 30 kw. furnace, in order to verify our results on this point.

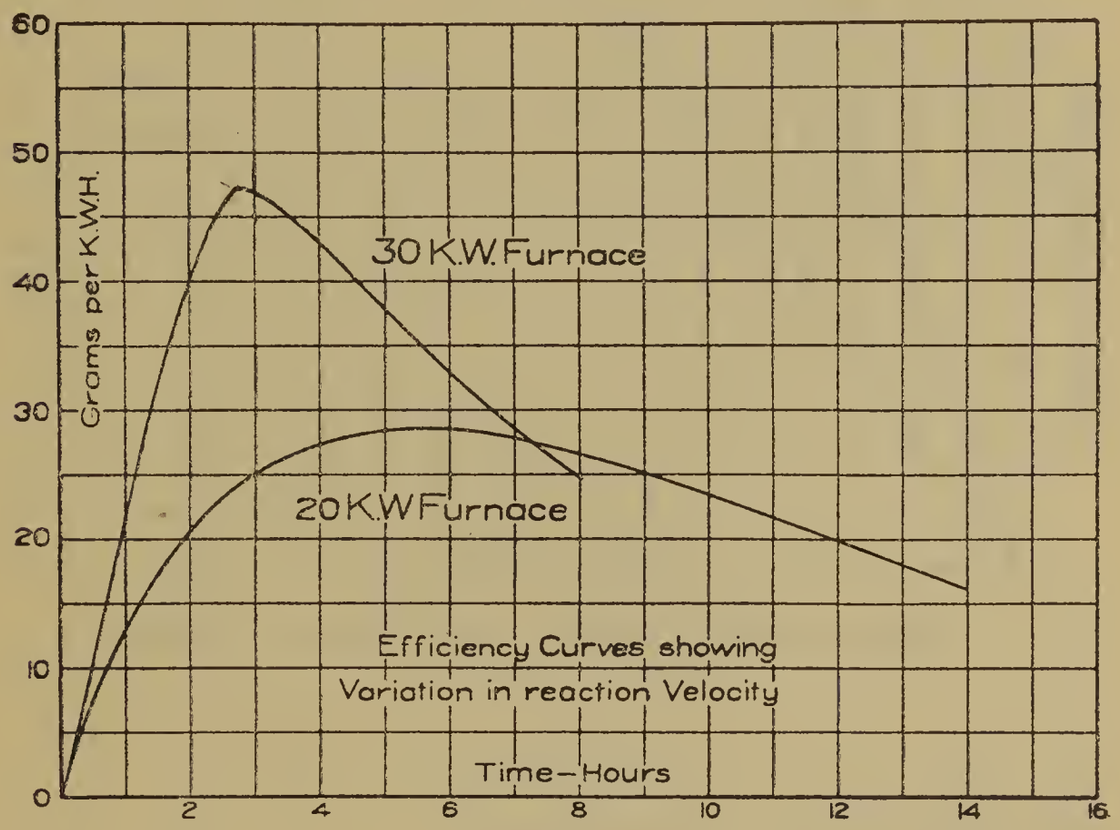


FIG. 5.

The curves showing the relative SiC yields for the two rates of heating, Fig. 6, make it at once evident that, the quality yield being equal, a 6-hour run at 30 kw. is cheaper than a 10-hour run at 20 kw. On the other hand, at the end of 6¾ hours the 20 kw. furnace is giving the same efficiency as the 30 kw. one, and shows a higher efficiency from that point on. This would indicate that for long periods of run the 20 kw. furnace would have the advantage, provided the efficiency of the 30 kw. furnace continues to fall off at the same rate.

With the furnace of the dimensions we used, 30 kw. is really

rather too much, as the bricks began to soften towards the end of the run. It is a very good size for a 20 kw. run and would probably work well at 25 kw.; but we have no data on this point.

In connection with these runs we have collected data in regard to heat losses with graphite electrodes and with carbon electrodes, but these will form the subject of another paper at some future time.

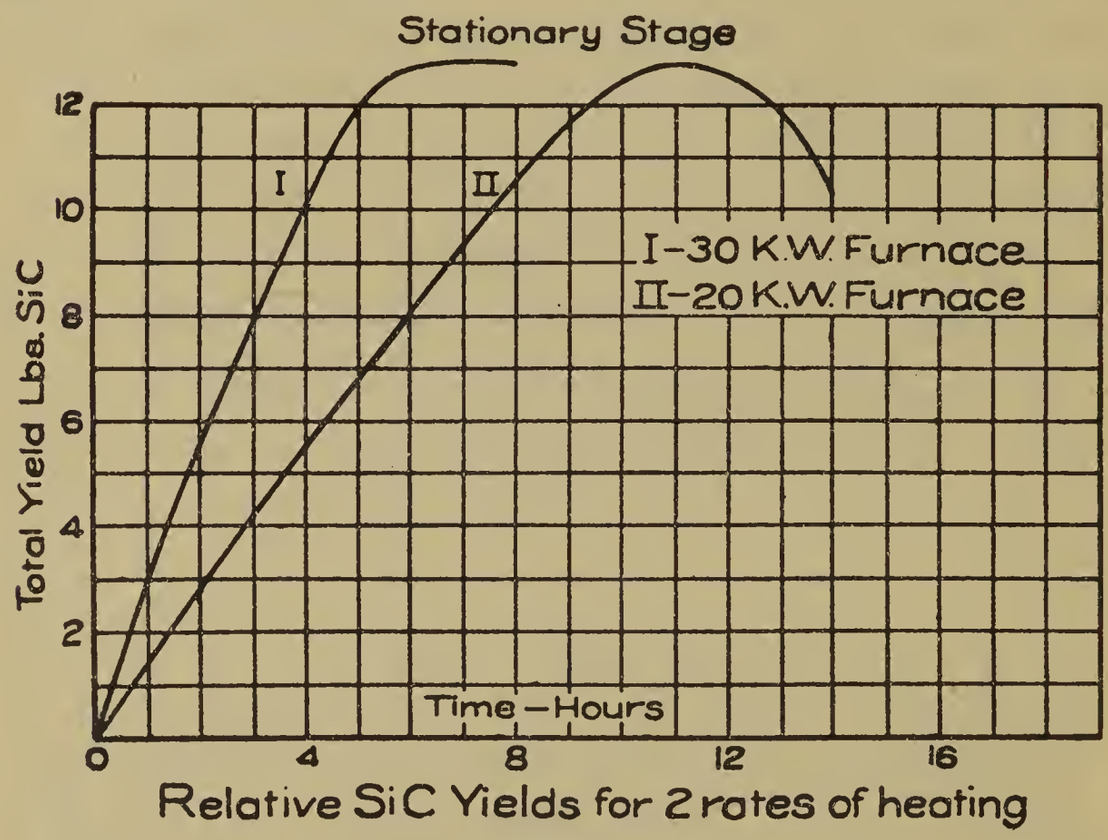


FIG. 6.

Conclusions.

The general results of this paper are:

1. A furnace has been devised in which it is possible to duplicate results with a satisfactory degree of accuracy.
2. We have made a study of yields in a 20 kw. and a 30 kw. furnace of specified dimensions, using a carbon core.
3. Curves are given for core temperatures during a run, and for temperatures in one other part of the furnace.
4. Curves are given for absolute yields of graphite, carborundum, and siloxicon for different lengths of run.
5. Curves are given for yield of carborundum per kilowatt hour under different lengths of run.

Cornell University.

DISCUSSION.

MR. L. E. SAUNDERS:—The general results of the paper are summed up in five paragraphs, and it is to be supposed that the purpose of the experiments is stated in those five paragraphs. It seems to me that there are no conclusions reached there that have not been published for a great many years. For instance, No. 1, "a furnace has been devised in which it is possible to duplicate results with a satisfactory degree of accuracy." For the last twenty-five years or so that has been done on a commercial scale. A study of the yields in small furnaces was made probably as long ago, with the results all published. So that I see very little in the paper here which has not appeared in print and been well known before.

MR. L. V. WALKER:—I would like to ask Mr. Saunders what his opinion of the stationary stage is in this work, and whether or not there is such a thing as a decrease in yields if the run be continued too long.

MR. SAUNDERS:—As applied to furnace of 20 or 30 kilowatts, I really could not make any statement at all, for my experience with those sizes is very limited. I regret to say that I am not permitted to discuss these questions as regards commercial furnaces. One thing that has been omitted here which would probably have been new to most people and would have been instructive is the calculation in every experiment of the watts per square inch of core area on which the efficiency of this type of furnace depends.

MR. W. D. BANCROFT (*Communicated*):—If I had realized that Mr. Saunders was such a purist as to style, I should of course have changed the objectionable first conclusion so that it would read that "a *small* furnace, etc." I had assumed—apparently erroneously— that a man would remember the title of a paper at least until he had finished reading it. Doubtless, Mr. Saunders is right in saying that results identical with ours

were published twenty-five years ago; but I should be grateful for the reference. It would have been helpful if Mr. Saunders had explained why the temperature gradient is so extraordinarily different in this particular small furnace from what it is in a commercial furnace. He cannot fail to have noticed the fact even though it was not referred to in the paper.

A Paper presented at the XXII General Meeting of the American Electrochemical Society, in Joint Session with Sections IIIa: Mining and Metallurgy, Xa: Electrochemistry, and XIb: Conservation, of the VIII International Congress of Applied Chemistry, in New York City, September 10, 1912. Prof. W. H. Walker in the Chair.

THE ELECTRICAL RESISTIVITY OF FIRE-BRICKS AT HIGH TEMPERATURES.

By A. Stansfield, D. L. McLeod, and J. W. McMahon.

INTRODUCTION.

Fire-bricks, and most refractory materials, are electrical insulators when cold, but, as is well known, at furnace temperatures they are partial conductors, and this affects their use in the construction of electrical furnaces. Hardly any data have been published, however, with regard to the electrical resistivity of these materials at high temperatures. This matter is of some importance with regard to the design of electric furnaces, because in many of these there is an opportunity for the electric current to flow in part through the heated walls of the furnace instead of merely through the resistor, or through the charge which is to be heated. Such leakage may not be harmful in some instances, but in others it may tend to overheat and melt the brick-work, and in any case it is desirable, when designing a furnace, to know the probable magnitude of this effect.

Another instance where a knowledge of the resistivity of furnace materials would be desirable is in designing a furnace like the Rodenhauser induction furnace, where the current is supplied to "pole pieces" and passes through a wall of refractory material before entering the steel in the furnace. In such a case it would be desirable to know the electrical resistance of the plate of refractory material separating the "pole piece" from the contents of the furnace.

The experiments here described were made by Messrs. McLeod and McMahon as an undergraduate research in the Metallurgical Department of McGill University, and the results, although incomplete, are published with the hope of calling more attention to this interesting and important subject.

APPARATUS.

The materials tested were Caledonia fire-brick, Star silica-brick, magnesite-brick and chrome-brick, the last three being obtained from Messrs. Harbison-Walker. Cylinders 2 inches in diameter and about 2½ inches long were cut from these bricks, the length of the cylinder being the thickness of the brick. These cylinders were supported, as shown in the figure, between discs of graphite of the same diameter, and contact was made between the cylinders and the disc by means of a paste of graphite and glue. In the first few experiments the apparatus was heated in a gas furnace, but this method of heating was

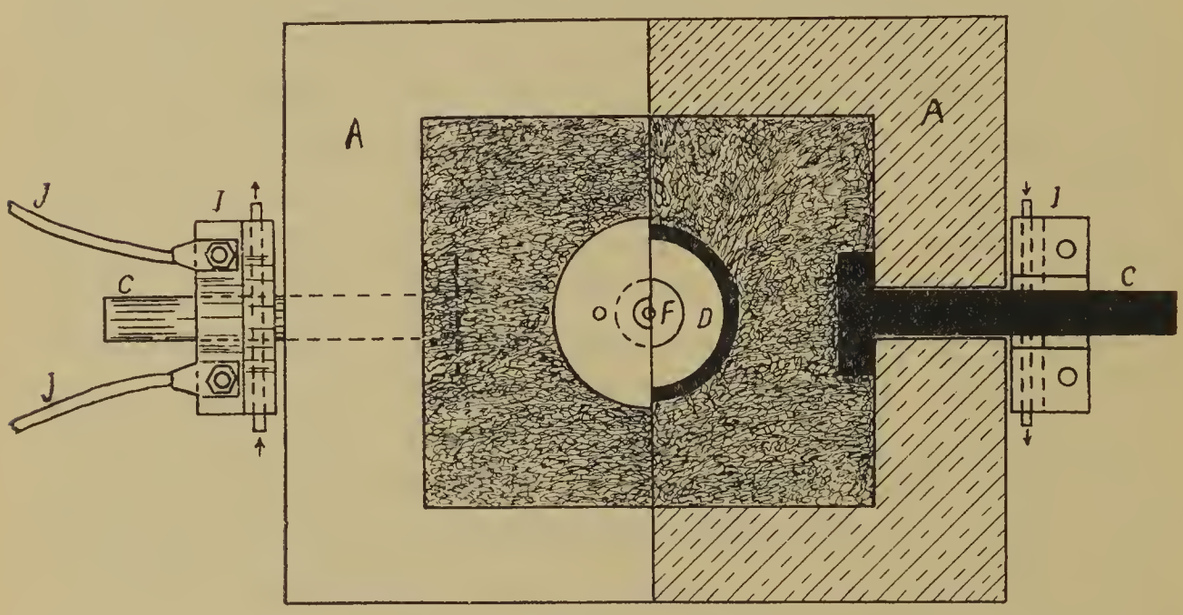


FIG. 1.

found unsatisfactory, and electrical heat was employed in the apparatus shown.

In the figures, F is the test-cylinder and E E are carbon electrodes supplying the testing current. Direct current was used at 110 volts, with a rheostat of lamps to avoid the danger of accident and to reduce the current flowing through the test-piece when the resistance became low. The current passing through F was read on an ammeter. To avoid any possible error through polarization, due to the use of a direct current, a reversing switch was used so that the current could be reversed in the test-piece before taking the reading. The testing current was supplied to the carbon electrodes E E by metal clamps, and the voltage

was read on a voltmeter connected to the same clamps. The resistance measured includes the resistance of the carbon electrodes E E, which would be about 0.13 ohm, and would represent a correction of 0.4 ohm to be deducted from the resistivities stated in the table. These figures also include the contact resistances between the ends of the test-pieces and the carbon discs. These resistances were made as small as possible, and were probably a small fraction of the whole resistance. The method adopted is somewhat crude from an electrical point of view, but it was considered essential that the construction of

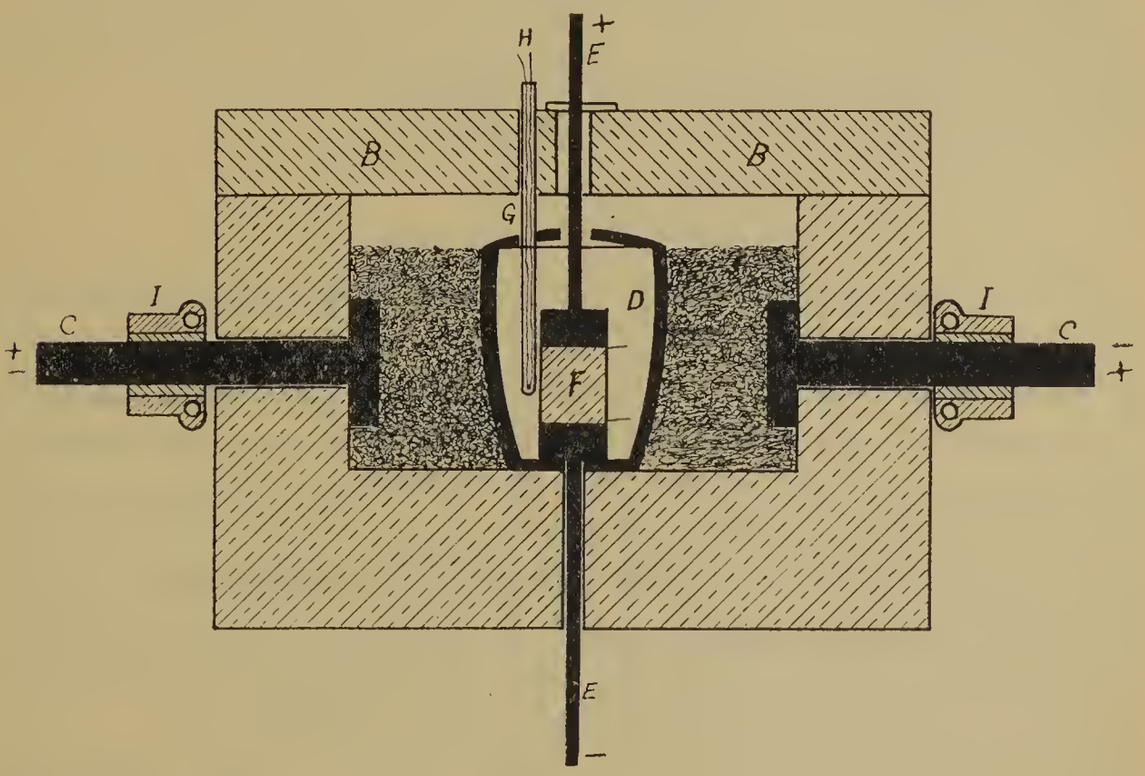


FIG. 2.

the apparatus should be as simple as possible in view of the high temperature at which the tests had to be made. The test-piece was enclosed in a graphite crucible D in such a way that the testing current could not be short-circuited through the graphite crucible or through the heated portion of the furnace walls. A thermo-couple pyrometer H, in a silica tube, was used to indicate the temperature of the test-piece. The furnace was filled around the crucible with broken graphite varying from ½ inch to ¼ inch in size. Alternating current was supplied by means of water-cooled electrode holders I to the 1½-inch elec-

trodes C C, having blocks of graphite on their ends for distributing the current. From 300 to 600 amperes at about 30 volts were used for heating the furnace, and any temperature up to about 1700° C. could be easily obtained. The voltage of the test current was about 100 at low temperatures, and dropped to 5 or 10 volts at the highest temperatures. The ammeter could be read to 0.01 ampere, and the largest current measured was about 1.2 amperes at about 5 volts.

The thermocouple was of platinum and platinum with 10 per-cent of rhodium. It was calibrated at the melting point of copper, 1083° C., and the melting point of the couple itself, which was taken as 1775° C. The calibration curve was assumed to be a straight line between these points.

RESULTS.

The results obtained from these experiments have been tabulated, and are also shown, in part, as curves. It will be seen from these that at 1500° C. the resistivity of all these materials is somewhat low. Comparing the results for the different materials, it will be noticed that the silica and magnesia-bricks, which approximate most closely to pure oxides, retain their insulating qualities to high temperatures, no considerable current being obtained below about 1300° C. The fire-brick and chrome-brick, on the other hand, which are more complex in composition, begin to conduct at considerably lower temperatures. At the highest temperatures observed, about 1550° C., the resistivities of all the bricks tested were about the same, being about 25 ohms for a one-centimeter cube. The accuracy of the readings was not very great, being limited by that of the ammeter for high resistivities and by that of the voltmeter for low resistivities. It is possible that the combined error would not be more than 5 percent or 10 percent for most of the readings, but increasing, in the case of the higher figures, above 6,000 ohms, to a maximum error of about 25 percent at 21,000 ohms. It is doubtful whether the higher temperature readings are to be depended on within about 20° C., although the relative error in the readings would be less than this. The results obtained for the chrome-brick are very peculiar. This was not noticed until it was too

late to repeat the observations, and they should therefore be regarded as subject to correction.

In connection with these results it is interesting to allude to a few figures which have already been published in this connection. Reference may be made to a paper by H. M. Goodwin[1] on the physical properties of fused magnesium oxide. The electrical resistivity of this oxide was tested and was found to be 380,000 ohms for a centimeter cube at 1,150° C., which was the highest temperature reached. Landolt & Börnstein give the resistivity of magnesia at 1,500° C. as 12,000 ohms for 1 centimeter cube, and that of zirconia as 1,200 ohms at 1,200° C.

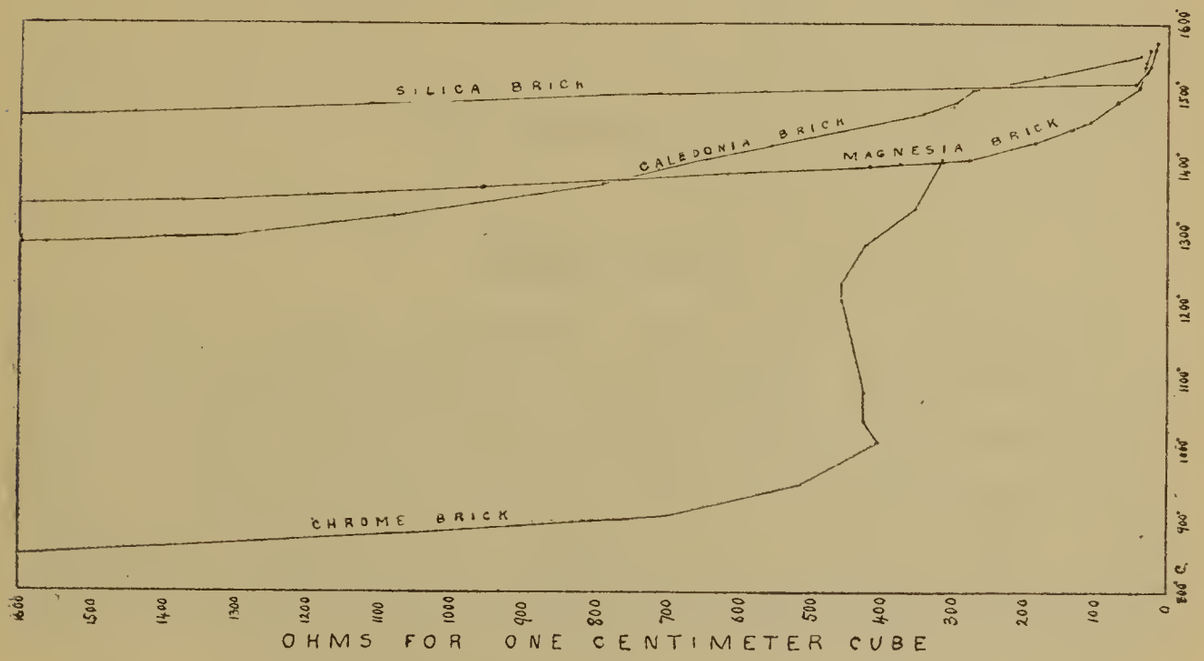


FIG. 3.

These figures are very much higher than we have obtained for fire-bricks, but it may be mentioned that MgO + 10% B_2O_3 at 1,250° C. has a resistivity of 83 ohms. On the other hand, porcelain at 1,000° C. has a resistivity of 330,000, according to Nernst-Reynolds, and Goodwin gives values of 1,000,000 ohms at 1,000° C. and 780,000 ohms at 1,100° C., which seem very high in view of the figures we have obtained for fire-brick.

The results give the averages of a number of tests which were in most cases quite concordant. It would be desirable to extend the work to higher temperatures and to use test-pieces of different dimensions.

[1] H. M. Goodwin, Trans. Am. Electrochem. Soc., 9, 80 (1906).

Electrical Resistivity.

Ohms for One Centimeter Cube.

Temperature	Caledonia Fire-brick	Silica Brick	Magnesite Brick	Chrome Brick
600° C.	21,000	....	....	....
700°	17,000	....	....	....
800°	13,000	....	....	2,800
900°	9,000	....	....	760
1,000°	6,600	....	....	420
1,100°	4,400	....	....	430
1,200°	2,300	....	....	450
1,300°	1,300	9,700	6,200	410
1,400°	690	2,400	420	320
1,500°	280	710	55	....
1,550°	60	22	30	....
1,565°	....	18	25	....

DISCUSSION.

Prof. Joseph W. Richards: Aluminium nitride is found to be a very refractory material, not decomposing below 2250° C., and possesses a low heat conductivity and a high electrical resistance, so that it can be used as an insulator at temperatures below 2000°. There seems to be evidence that amongst the various nitrides may be found the solution of this problem of highly refractory materials with low electrical conductivity.

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MELTING POINTS OF FIRE BRICKS.

By C. W. Kanolt.

We are accustomed to thinking of a melting point as a temperature at which a substance changes from a condition in which it does not flow perceptibly under its own weight to a condition in which is flows readily. However, no rational definition of the melting point can be based upon this conception. For example, when glass is heated the transition from its ordinary condition to a distinctly fluid condition is a very gradual one and occupies a range of several hundred degrees. Some other substances which possess perfectly definite temperatures of transition to a fluid phase undergo changes resembling fusion at lower temperatures. Solids in general become softer when heated; they may become so soft as to yield to their own surface tension, with the result that sharp corners are rounded off. Rutile in its natural, slightly impure condition melts at about 1700° C. The melting point is very definite, there being a sharp transition from a rather soft solid to a liquid of low viscosity, with a considerable absorption of heat. Yet at temperatures 100° or more below the melting point corners are rounded off and small particles become sintered together. The sintering of clay is probably a similar phenomenon of surface tension. Clay exists generally in the form of extremely fine particles, its unusually slight solubility in water accounting for this condition. Fine particles are more readily united by surface tension than large ones.

A melting point can be precisely and rationally defined only as the temperature at which a crystalline or anisotropic phase and an amorphous or isotropic phase of the same composition can exist in contact in equilibrium. In harmony with this, one might define a solid as a crystalline substance, and a fluid as a substance not crystalline; however, these definitions of solid and fluid would lead to results quite different from our ordinary conceptions, as

they would require us to consider glass, even silica glass, as a fluid, and certain "anisotropic liquids" whose viscosities are even less than that of water, as solids. Perhaps it is better to leave solid and liquid or fluid as general terms without precise definitions.

While the above definition of melting point is satisfactory for the case of a pure substance, so complex a mixture as an ordinary fire brick usually has no single definite melting point according to this definition, since several anisotropic phases may be present, all differing in composition from the isotropic phase produced by fusion. We can, then, only select the temperature at which the transition from a rigid to a fluid state seems most distinct, and can call this the melting point only by convention.

In the case of fire bricks the transition temperatures so found are fortunately sufficiently definite to make their determination of practical value. I have taken as the melting point the lowest temperature at which a small piece of the brick could be distinctly seen to flow. Experiments showing the degree of definiteness of this temperature will be described.

The melting point of a brick is, of course, not the only property to be considered in determining its fitness for a given purpose. Its crushing strength cold, its behavior under load conditions when heated and its resistance to fluxes may all be important. The present paper deals only with melting points.

A large number of the brick samples tested were kindly furnished by Dr. A. V. Bleininger, being identical with samples tested by Bleininger and Brown[1] under load conditions at 1300° C., this work being carried out at the Pittsburgh testing station of this bureau, which station was at that time the technologic branch of the United States Geological Survey. The chemical composition, crushing strength cold, porosity and density of these samples are given by Bleininger and Brown. They also determined the Seger cone numbers corresponding to the softening temperatures of the bricks.[2]

It is difficult to interpret results obtained with Seger cones in terms of actual temperatures, for it has been shown by Simonis[3]

[1] Bureau of Standards Technologic Papers, No. 7, 1912.

[2] See also Hofman and Demond: Trans. Am. Inst. Mining Eng., **24**, 42 (1894). Hofman: Trans. Am. Inst. Mining Eng., **25**, 3 (1895); **28**, 435 (1898). Hofman and Stroughton: Trans. Am. Inst. Mining Eng., **28**, 440 (1898). Gary: Mitt k. tech. Versuchsanstalten, **14**, 63 (1896). Jochum: Thonindustrie Zs., **27**, 764 (1903). Weber: Trans. Am. Inst. Mining Eng., **35**, 637 (1904).

[3] Simonis: Thonindustrie Zs., **32**, 1764 (1908).

that the falling over of Seger cones, of certain numbers at least, depends not only upon the temperature, but also to a large extent upon the rate of heating. This observation has been confirmed in this laboratory, using the cone numbers having softening temperatures in the same range as fire brick, and it has happened that in many cases the melting point of a fire brick, defined as stated above, is more definite than the softening temperature of the corresponding Seger cone. It has, therefore, appeared preferable to use a more direct and more accurate method of determining temperatures.

The experiments were conducted in an Arsem graphite resistance vacuum furnace[4] (Fig. 1). In some preliminary experiments upon fire bricks samples were heated in graphite crucibles and exposed to such gases as might remain in the furnace. Although the pressure was kept as low as 2 mm. of mercury, there was still a slight reducing action upon the brick, and some samples were blackened superficially. Subsequent work has shown that the action was insufficient to produce any very great difference in the results, but, as a matter of precaution, the specimens were protected by a refractory tube (*A*, Fig. 1) being placed upon a bed of white alundum (fused alumina) in the bottom of the tube. This tube was supported by the brass collar, *B*, in which it was made to fit tightly by winding with asbestos string, or otherwise, and which was soldered to the lead gasket by which the joint, *C*, in the top of the furnace was made air tight.

The refractory tubes were made of a mixture of 72 percent kaolin and 28 percent alumina, these being the proportions for the formation of sillimanite, $Al_2O_3.SiO_2$. According to Shepherd and Rankin[5] pure sillimanite melts at 1811°. The sillimanite tubes were found to melt at about this temperature. Kaolin tubes were used for some samples of relatively low melting points. Either sillimanite or kaolin tubes were used with all fire bricks melting below 1800°. The chromite and magnesia bricks were melted in graphite crucibles without protecting tubes. The experiments were made rapidly and the graphite had little action on the samples until after fusion had occurred and the melting point had been determined. Magnesia tubes may be used in place

[4] Arsem: J. Am. Chem. Soc., 28, 921 (1906); Trans. Am. Electroch. Soc., 9, 153 (1906).

[5] Shepherd and Rankin: Am. Jour. Sci., 28, 301 (1909).

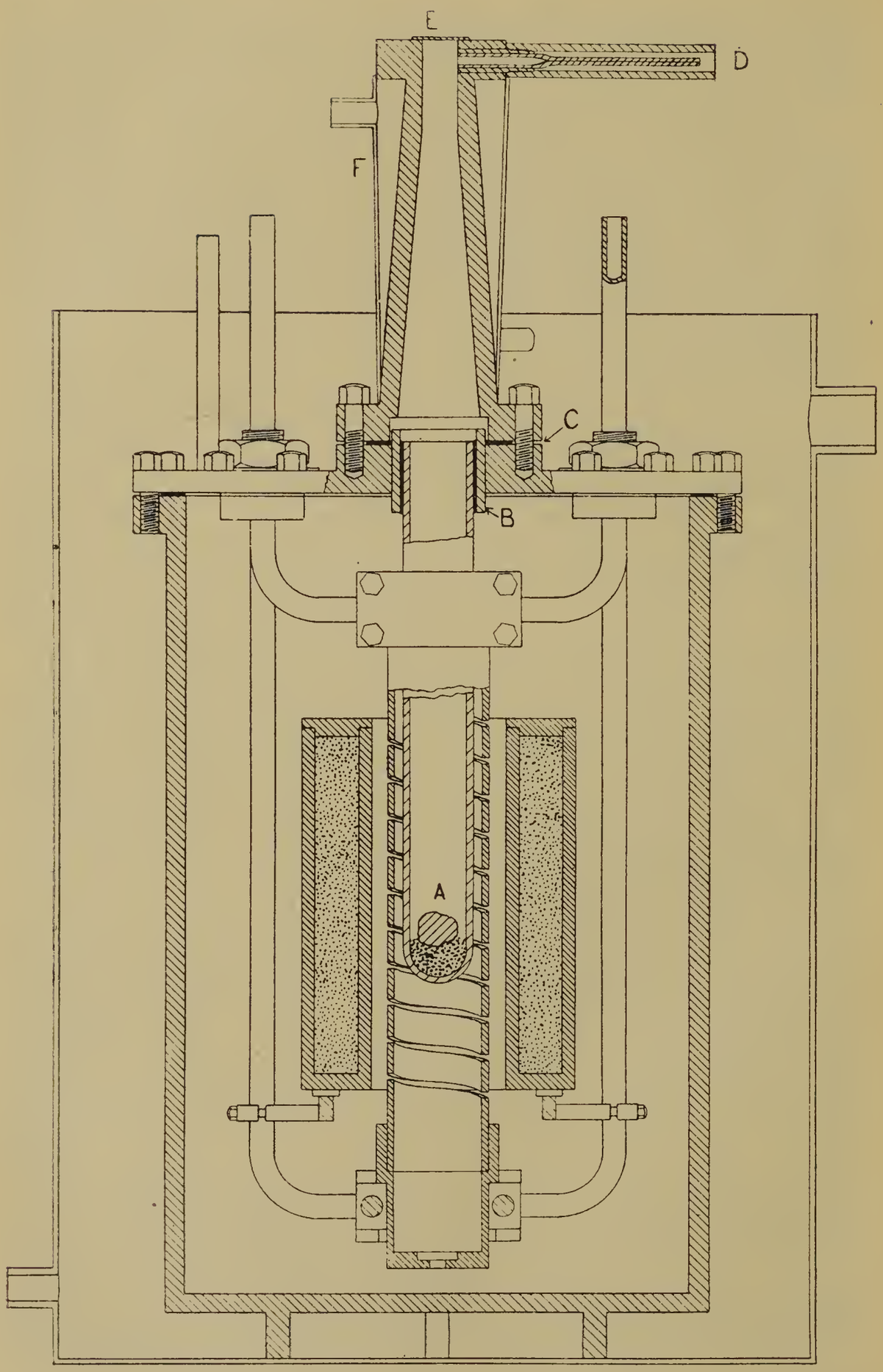

FIG. 1.

of sillimanite tubes, and they have the advantage of a higher melting point; but all magnesia tubes that have been tried have been found to be very easily cracked by changes of temperature, and to be so porous as to afford little protection from the gases of the furnace. When a sillimanite or kaolin tube was used, 20 to 30 minutes was consumed in heating the furnace to a little below the melting point of the sample. This initial heating could be performed much more quickly, as far as the furnace is concerned, but more rapid heating would be likely to crack the tube. When the temperature had nearly reached the melting point it was raised much more slowly. When these protecting tubes were used the samples showed only very slight signs of reduction. In certain experiments made with this apparatus (for example, the determination of the melting point of platinum as a check upon the work) it was desirable to still further diminish the chances of the presence of reducing gases. This was accomplished by the device shown at *D* in Fig. 1, which consists of a glass tube drawn out into a fine capillary and leading into the furnace. An outer brass tube protects the capillary. This capillary admits a slow current of air to the inside of the refractory tube, and the air passes out through the pores of the tube into the interior of the furnace. By working the vacuum pump continually the pressure in the furnace was kept down to a few millimeters of mercury, in spite of the influx of air. This process was, of course, injurious to the graphite heater, but several such experiments could be made with one heater before it was burned out.

While the sample was being heated it was observed through the window, *E*, at the top of the furnace. A glass window was used here in place of the mica window provided by the makers of the furnace. The glass was attached by a mixture of rosin and beeswax. To keep this material cool an additional water jacket, *F*, was applied to the part of the furnace projecting above the water of the tank.

The temperatures were determined by means of a Morse optical pyrometer of the Holborn-Kurlbaum type,[6] which was sighted vertically downward through the furnace window. The current

[6] Holborn and Kurlbaum: Sitzber. d. k. Akad. d. Wissensch. zu Berlin, June 13, 1901, p. 712, Ann. d Phys., **10**, 225 (1902). Waidner and Burgess: Bull. Bureau of Standards. **1**, No. 2, (1904). Mendenhall: Phys. Rev., **33**, 74 (1911). Henning: Zs. f. Instrumentenkunde, **30**, 61 (1910).

in the pyrometer lamp was measured with a Siemens and Halske milliammeter with a shunt. This instrument was calibrated several times, and its very small temperature coefficient was taken into account. Its readings are certainly reliable to 0.001 ampere and probably to 0.0005 ampere.

The carbon-filament pyrometer lamp was one of the standard lamps of the bureau, thoroughly aged, and had been accurately calibrated by several observers before the beginning of the investigation, and again, by a different method, toward its close. In the first calibration it was sighted into a platinum-resistance furnace in which black-body conditions obtained, and the temperature of which was measured by platinum : platinum-rhodium

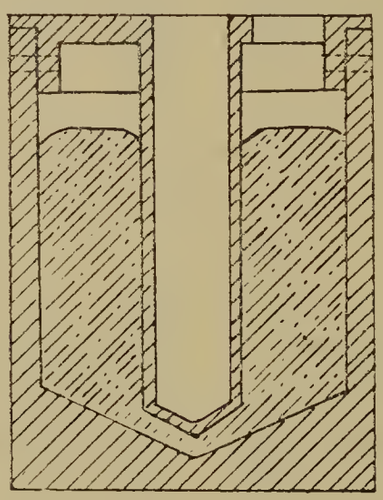

FIG. 2.

thermocouples. These thermocouples had been calibrated against the freezing points of pure metals. In the second calibration the lamp was calibrated against the freezing points of metals directly, without the intermediation of thermocouples. The metals used were copper, silver, and the copper-silver eutectic, which freeze at 1083°, 961°, and 779°, respectively. These were placed in Acheson graphite crucibles of the form shown in Fig. 2, about 100 grams of metal being used in each. The pyrometer was sighted downward into the central graphite tube, of which the inside diameter was 6 mm. and the wall thickness 1 mm. The crucibles were heated or cooled gradually, while observations were made every 10 to 20 seconds, and the resulting heating or cooling curves were plotted. A typical curve is shown in Fig. 3.

In this diagram a change of temperature of 1° corresponds to a change of current of about 0.0005 ampere. By means of the three known temperatures, the relation between the current in the lamp and the temperature was expressed in the form, $C = a + bt + ct^2$.

This method presented two possible sources of error to be especially considered, namely, the conduction of heat along the inner graphite tube, and the departure of the interior of this tube from black-body conditions. If the conduction of heat along the tube introduced appreciable error, the observed temperatures would be too high with rising temperature, when the furnace

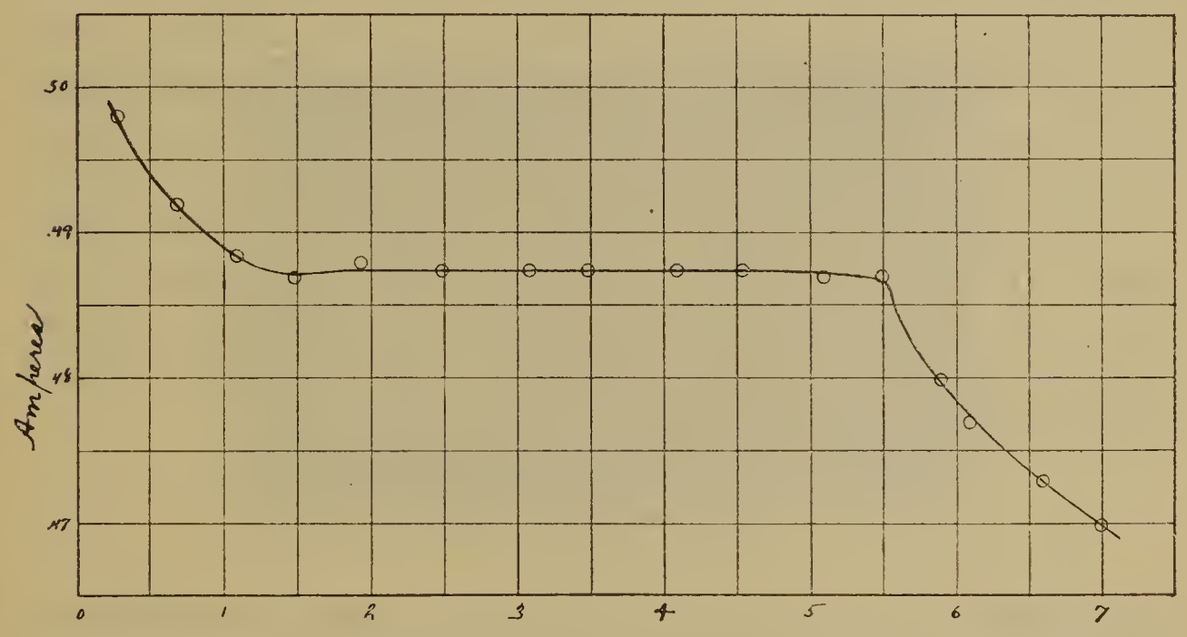

FIG. 3.

heater would be hotter than the metal, and too low with falling temperature, when the reverse would be true. The fact that the results from the heating curves obtained with copper and silver were in very close agreement with those from the cooling curves shows that the errors from conduction are negligible; and these and numerous other observations have indicated that the interior of such a tube, when made of graphite, which is itself nearly perfectly black, is a very good black body. Using the copper-silver eutectic, somewhat unsatisfactory results were obtained with heating curves, the trouble appearing to be in the behavior of the alloy rather than in the temperature measurement. In this case only cooling curves were used for the calibration. The calibration

of the lamp at this temperature is relatively unimportant, since none of the melting points here given correspond to a lamp temperature below the melting point of silver. The results of this calibration agreed with those obtained by the first method within 1°, from 700° to 1300°, which includes all lamp temperatures used in this work. Near the close of the investigation the pyrometer lamp was accidentally overheated, and it was necessary to recalibrate it. This time, only the cooling-curve method was used.

As the melting points to be measured were above the working limit of the pyrometer lamp, an absorption glass was interposed between the pyrometer and the furnace. This glass was calibrated as follows: In the Arsem furnace was placed a graphite crucible, the interior of which, when the furnace was hot, furnished a field of very uniform brightness. A steady current was passed through the furnace and the temperature allowed to become stationary. The temperature was then measured with the pyrometer, and also the apparent temperature as observed through the absorption glass. If T_1 is the absolute temperature, observed without the glass, and T_2 is the apparent absolute temperature observed with the glass, we have the following relation, which is easily deduced from the Wien radiation law:

$$\frac{1}{T_2} - \frac{1}{T_1} = A$$

The constant, A, was determined in this way with several different furnace temperatures, and the results were in close agreement. The mean value of A was 0.0002249. The values of the constants of Wien's law do not enter into the work.

The glass furnace window absorbed and reflected a small amount of light, and it was necessary to apply a correction for this. The constant of this glass was determined in the same way as that of the absorption glass, and was found to be 0.0000040. The correction in degrees depends, of course, upon the temperature; it is about 15° at the melting point of ordinary fire brick.

As a check upon the whole apparatus, a determination of the melting point of platinum was made. A piece of platinum foil was placed within two magnesia tubes, one within the other, in the place of the single tube shown at A (Fig. 1), and a slow current of air was admitted at D. Fairly good black-body conditions

were obtained, but the platinum was faintly visible. The observed melting point was 1750°. The value accepted by the Bureau of Standards as the melting point of platinum is 1755°. After the pyrometer lamp had been overheated and recalibrated, this test was repeated. In place of magnesia tubes, tubes of a mixture of magnesia and alumina,[7] obtained from the Königliche Porzellan-Manufactur, Berlin, were used. These were found to be more satisfactory than magnesia tubes, being much less porous and less easily cracked. The material softens at a little above the platinum point. Using a single tube the value 1746° was obtained, with two tubes 1750°. Tests were also made in an iridium tube furnace, where there was no possibility of a reducing atmosphere.

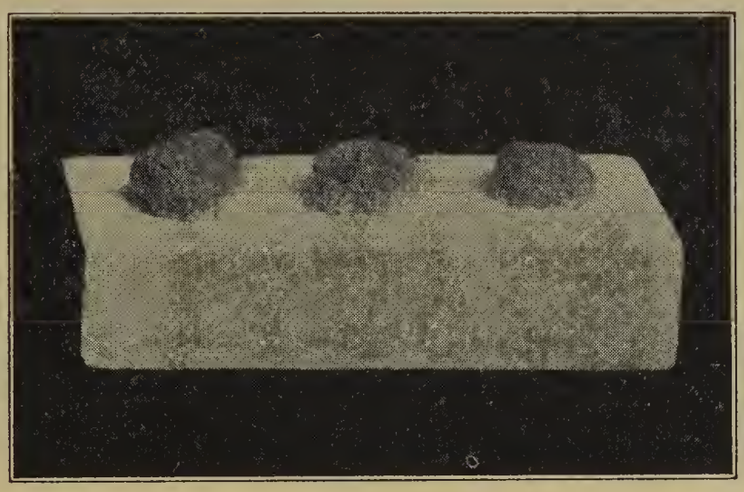

FIG. 4.

So good black-body conditions were obtained that the platinum was quite invisible. A piece heated to 1747° and removed was found not melted; one heated to 1759° and removed was found melted.

The use of the optical pyrometer depends upon the assumption that the object sighted upon emits black-body radiation. This is the case if the object is within a vessel at uniform temperature, and is viewed through a relatively small opening in the vessel. This can readily be accomplished in the apparatus used, but under such conditions it would be impossible to distinguish the sample, owing to the uniform brightness of the sample and its environs. In practice, the sample was placed slightly below the hottest part of the furnace, in such a position as to be barely distinguishable.

[7] Heinecke, Zs. angew. Ch., **21**, 687 (1908).

This requires only a temperature difference of about 5°. When the temperature of a sample had almost reached the melting point, the temperature was raised more slowly and the sample was observed continually. When it was seen to melt, a final temperature measurement was made and the heating current was immediately stopped, thus preventing the temperature from rising any higher. The observation was then verified by an examination of the sample after its removal from the furnace.

An idea of the degree of definiteness of the melting points may be obtained from Fig. 4 and Fig. 5, in which are shown samples which have been heated to successively higher temperatures. Fig. 4 may be taken to represent the usual degree of

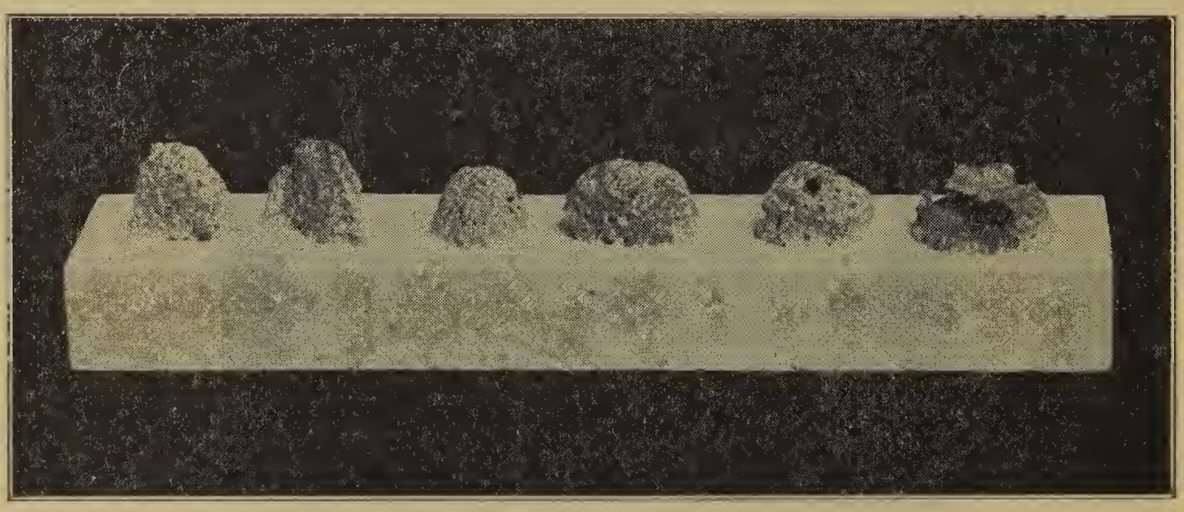

FIG. 5.

definiteness. The sample heated to 1680° C. appears unaffected; that heated to 1695° shows very slight signs of fusion; that heated to 1705° is completely fused; 1705° was taken as the melting point. Fig. 5 shows perhaps the least definite melting point found. Complete fusion occurred as 1620°, but there was partial fusion at considerably lower temperatures; 1600° was taken as the melting point.

Near the melting point samples were heated at the rate of about 10° per minute. This rate of heating was quite slow enough, as a temperature measurement can be made in a few seconds, and a slower rate of heating near the melting point was found to give the same results. The entire time required for heating a sample from room temperature to its melting point was 30 to 40 minutes. Experiments were made to determine

whether samples could undergo any change in melting point as the result of heating in the vacuum furnace. Samples of various kinds were heated in the furnace to about 1550° for about six hours, and their melting points were then determined. The results are given in Table I.

TABLE I.

Sample	Material	Determinations of Melting Point Without Previous Heating	Determinations of Melting Point After Six Hours Heating
		Degrees	Degrees
14	Fire clay	1635	1655
		1630	1655
27	Fire clay	1600	1635
		1610	1630
		1600	1635
		1585	1640
		1595	....
48	Fire clay	1710	1705
		1705	1695
		1705	....
		1700	....
		1705	....
20	Bauxite	1740	1740
		1745	1730
41	Silica	1705	....
		1700	....
		1695	1695
		1695	1700

It appears from the table that Nos. 14 and 27, which are bricks of low melting point, melted at a somewhat higher temperature after long heating, while the other bricks were unaffected. The melting point of No. 27 is less definite than that of most bricks. This increase of melting point might be accounted for upon the assumption that the brick consisted of two materials existing in distinct particles, one sort having a lower melting point than the other, these two materials becoming run together after long heating near the melting point, producing a material of higher melting point than that of the more fusible of the original materials. The appearance of samples of No. 14 and No. 27 after heating for a short time to near the melting point supports this explanation. Sample No. 27 is shown in Fig. 5. After the six hours' heating they appeared more uniform. Long heating in a

vacuum would tend to vaporize the more volatile constituents of the brick, and this might produce an appreciable increase of melting point.

The most common fire brick are those made of clay, of which the essential ingredient is kaolin, $Al_2O_3.2SiO_2.2H_2O$. Shepherd and Rankin[8] found that the only compound of alumina and silica that can exist in the neighborhood of the melting points is sillimanite, $Al_2O_3.SiO_2$. It follows that clay when near its melting point is no longer a single compound, but a mixture of $Al_2O_3.SiO_2$ and SiO_2. Hence the melting point of pure kaolin, like that of fire brick, can not be expected upon theoretical grounds to be perfectly definite, but fairly definite results are obtained when the visible flow is taken as the criterion of fusion, as in the case of fire brick. Two samples of white kaolin, one English, the other probably English also, both melted at 1740°. A sample of brownish-white German kaolin melted at 1735°. Therefore the highest melting point that can be attained in brick containing nothing more refractory than kaolin is 1740°. When an excess of alumina is present, as in bauxite brick, the melting point may be higher.

A few brands of silica brick were tested. Pure silica melts at about 1600°.[9] However, the fused silica possesses such extreme viscosity near the melting point that it does not flow or change shape distinctly untll considerably higher temperatures are reached. I have obtained 1750° as the *apparent* melting point of pure silica, *i. e.*, the temperature at which it flows distinctly. This temperature, however, is naturally a very indefinite one. The temperature at which silica bricks flow distinctly is more definite.

Bauxite brick are made from bauxite, $Al_2O(OH)_4$, containing usually considerable quantities of other material. Bauxite, of course, becomes converted to alumina, Al_2O_3, when heated. Pure alumina melts at about 2010°.[10] None of the bauxite bricks examined approached this melting point. A single sample of bauxite was tested and found to melt completely at 1820°, the centers of the nodules melting at 1790°. A sample of bauxite clay melted at 1795°.

One brand of magnesia brick was examined and found to melt

[8] *Loc. cit.*

[9] Day and Shepherd: J. Am. Chem. Soc., **28**, 1089 (1906).

[10] A paper on the melting points of pure refractory oxides is in preparation.

at 2165°. The melting point of pure magnesia is more or less in doubt at present. It is to be expected that it would be higher than that of the impure magnesia brick. This brick contained a large quantity of iron, and was of a dark brown color. When heated for a few minutes to near its melting point it became white. This occurred both in the electric vacuum furnace and in an oxy-hydrogen flame. It might result either from the vaporization of the iron, or from the formation of a colorless compound of iron and magnesia. An analysis of the specimens has shown that the heated samples contain much less iron.

One brand of brick made from chromite, $FeO.Cr_2O_3$, was examined. It was found to melt at 2050°. A sample of natural chromite from a different source melted at 2180°.

Silicon carbide, SiC, has been used as a refractory material. At very high temperatures it decomposes without melting. Tucker and Lampen[11] state that it decomposes at 2220°. Results in close agreement with this have been obtained by Gillett[12] and by Saunders.[13] This is undoubtedly correct for decomposition under ordinary conditions, but silicon carbide can be heated for a short time to much higher temperatures without complete decomposition. It was thought that by very rapid heating it might be possible to reach the melting point of the silicon carbide before decomposition was complete, although such a melting point would probably have only theoretical interest. With this object, a few grams of silicon carbide were placed in a graphite crucible, which was placed in a second larger graphite crucible to give more uniform temperature, and the whole was heated in an arc furnace at atmospheric pressure, the temperature being measured by sighting the optical pyrometer through a narrow graphite tube inserted in the top of the crucible. A temperature of 2700° or more was reached and was maintained for a few minutes. The silicon carbide was about half decomposed, leaving a residue of carbon, but showed no indication of fusion.

The results for fire brick will be found in Table II. Samples 1 to 26 are identical with the samples of the same numbers studied by Bleininger and Brown.[14] All the bricks tested were made in

[11] Tucker and Lampen: Jour. Am. Chem. Soc., **28**, 853 (1906).
[12] Gillett: Jour. Phys. Chem., **15**, 213 (1911).
[13] Trans. American Electrochemical Society, **21**, 425 (1912).
[14] *Loc. cit.*

the United States. Each melting point given is the mean of at least two determinations. The mean of the melting points of the 41 samples of fire-clay bricks is 1649°.

TABLE II.

Melting Points of Various Bricks.

Sample	Melting Point
Fire-clay brick:	
1	1630
2	1635
3	1605
4	1605
5	1705
6	1705
7	1700
8	1700
9	1675
10	1710
11	1660
12	1555
13	1635
14	1630
15	1655
17	1650
21	1615
22	1640
23	1660
24	1660
25	1715
26	1695
27	1600
28	1695
29	1595
30	1560
31	1600
32	1650
33	1655
34	1570
35	1650
Fire-clay brick—*Continued:*	
36	1590
37	1650
38	1660
47	1725
48	1705
49	1715
53[16]	1635
54[16]	1635
55[16]	1685
56[16]	1605
Bauxite brick:	
19	1760
20	1740
44	1720
45	1785
46	1720
50	1665
51	1565
52	1590
Silica brick:	
39	1700
40	1705
41	1700
Chromite brick:	
42	2050
Magnesia brick:	
43	2165

The analyses of a large number of the fire-clay bricks studied are available,[15] but it does not seem possible to establish any very definite relation between composition and melting point. Since the bricks contain about eight different constituents in quantities sufficient to affect the melting point, and since the melting point

[15] Bleininger and Brown, *loc. cit.*

[16] Samples 53, 54, 55, and 56 are of the same brands as 4, 9, 7, and 17, respectively, but from different lots.

may also be affected by lack of homogeneity in the material, it is obvious that a prediction of the melting point upon the basis of a chemical analysis would be uncertain. If the melting points are compared with the results of tests under load conditions at 1300°,[17] it is evident that there is little relation between the two.

SUMMARY.

1. The melting points of 54 samples of fire brick, including fire-clay, bauxite, silica, magnesia, and chromite brick, have been determined in an electric vacuum furnace, the temperature being measured with an optical pyrometer (Table II).

2. The following melting points of materials important in the manufacture of fire brick were determined:

	Deg.		Deg.
Kaolin	1740	Bauxite	1820
Pure alumina	2010	Bauxite clay	1795
Pure silica[18]	1750	Chromite	2180

3. An improved method of calibrating the Holborn-Kurlbaum optical pyrometer is described.

Mr. H. P. Greenwald and Mr. S. E. Moore have rendered efficient assistance in carrying out this work.

[17] Bleininger and Brown, *loc. cit.*

[18] This is not the true melting point but represents approximately the temperature at which silica flows distinctly.

Bureau of Standards,
Washington, June 15, 1912.

A paper presented at a Joint Meeting of the American Electrochemical Society, the American Institute of Mining Engineers and Sections "Electrochemistry" and "Metallurgy" of the Eighth International Congress of Applied Chemistry in New York City, September 7, 1912. Professor W. Lash Miller in the Chair.

HEAT LOSSES IN FURNACES

By F. A. J. FitzGerald.

In any kind of furnace the question of preventing the loss of heat is important, for no matter how the heat is obtained it costs something, and consequently, other things equal, that furnace is most desirable which uses the greatest percentage of the total heat generated for the particular object in view. In a furnace which uses electricity for the generation of heat the importance of preventing losses of heat is very much greater than in any other. To generate 1,000 kilogram calories requires an expenditure of 1.16 kilowatt hours, and consequently the cost per calorie is always expensive when electricity is used for heating.

In heating any material in a furnace a general rule is that the generation of heat should be as rapid as possible. In any given furnace the heat losses may be expressed as so many watts, and, therefore, the longer it takes to heat the furnace charge the greater the losses will be. Suppose that a furnace contains a charge to be heated to 1500° C., and that the average loss of heat is at the rate of 100 kilowatts, then if the process of heating the charge takes 1 hour the losses will amount to 100 kilowatt-hours; but if by using a more rapid generation of energy the charge can be heated in 30 minutes the losses will amount to 50 kilowatt-hours.

An example from experiments on a certain process may be given to illustrate this point. The problem was simply to heat a furnace charge to a certain temperature, and experiments were made to determine the effect of increasing the rate of generation of energy and comparing the kilowatt-hours required to heat a given charge. Here are typical results:

Rate of generation of energy	Energy per kilogram of product
88 kilowatts	1.7 kw.-hours.
93 kilowatts	1.6 kw.-hours.

Thus by increasing the rate of generation of energy by 5.7 per-cent the energy consumption was reduced 5.9 percent.

This particular example is only a laboratory scale experiment, but it serves to illustrate the point that in the design of an electric furnace one of the first things to consider in avoiding heat losses is to make the rate of heat generation per unit volume of charge as high as is compatible with other considerations, for in this way the saving of heat losses may be largely prevented. In the example given above the actual saving involved, working commercially and expressed in money, amounts to $1,250 per year.

Another point of great importance in furnace design in order to avoid heat losses is to keep the external surface of the furnace as small as possible. This is so very obvious that it seems almost an impertinence to mention it, but anyone who will take the trouble to study commercial furnaces of various sorts will find that this very point by no means receives the attention it deserves. Moreover, there does not appear to be any published information on what may actually be done in this way, so that the results of an actual experiment will be of interest.

In a resistance furnace using 746 kilowatts the charge was heated to a temperature somewhat above 2000° C., and maintained at that temperature for some hours. The furnace as originally constructed had an outside surface of 80 square meters, excluding the foundation. The design was afterwards changed so that the outside surface was 53 square meters. Determinations of the energy consumption per kilogram with the two designs of furnace give the following results:

Surface of Furnace	Energy per kg. of product
80 square meters	6.1 kilowatt-hours.
53 square meters	5.0 kilowatt-hours.
Reduction 34 percent	Reduction 18 percent.

Having done all that is possible in the way of perfecting the design of the furnace so as to avoid unnecessary heat losses, the final step is to provide the best heat insulation possible. Heat losses occur in various ways, but experience seems to show that the most serious losses are through the furnace body. Here the heat escapes in three ways: (1) Conduction, (2) convection, (3) radiation. It is highly desirable that all these methods of loss should be studied, but at the present time the necessary data are lacking. A study of each source of heat loss is difficult and will involve much time.

In view of these considerations it was thought desirable to make experiments as to the relative heat loss which occurs with various materials, some commonly used in furnace construction and some especially made for heat insulating purposes.

In order to do this, furnaces were constructed which have been described in detail elsewhere.[1] These consisted essentially of hollow cubes with external sides of 230 mm. while the hollow spaces were cubical with sides of approximately 110 mm., so that the thickness of the walls of the hollow cubes were 60 mm. The furnaces were supported on knife edges so that all sides were exposed to the air. Through small holes in the furnaces, wires entered to carry electric current to resistors of nichrome wire, and other holes in the furnace permitted the insertion of a thermocouple, by means of which the interior temperature could be determined.

In making an experiment a current was passed through the resistor and so regulated that the temperature was maintained constant. When equilibrium was reached the temperature and rate of generation of energy were noted, this giving the amount of heat escaping through the furnace walls at that temperature. The results of several experiments are given in the following table:

[1] These Transactions, **20**, 281 (1911).

TABLE.

Temperatures	°C inside furnace			Remarks
	500	700	800	
	Watts Lost	Watts Lost	Watts Lost	
Fire brick 1	460	760	910	Good quality.
Fire brick 2	485	780	950	Good quality.
Fire brick 3	425	705	860	Cheap brick.
Fire brick 3 with insulating jacket 25 mm. thick.	180	315	400	Special asbestos insulation.
Fire brick 4	430	685	810	
Fire brick 4, painted with lampblack	455	720	865	
Fire brick 4, painted with aluminum	370	600	725	
Silica brick	565	920	1100	Extrapolated from 800°. At 400° C. loss was 580 watts.
Magnesia brick	860	...	...	
Red building brick	280	460	565	
Insulating building brick	245	380	460	
Kieselguhr brick	130	220	275	

In the first column are given the materials of which the furnace was constructed, and in the second, third and fourth columns the heat losses at 500° C., 700° C. and 800° C., respectively.

It is interesting to note in this table the effect of the nature of the outside surface of the furnace on the heat losses in the case of fire brick 4. It also appears that silica and magnesia brick are far from satisfactory insulators, and if they must be used in furnace construction on account of their refractory qualities, they should be backed up with a better heat insulator.

Red building brick and the special heat-insulating brick are fairly good insulators, but by no means as good as the kieselguhr brick. A comparatively thin jacket of specially prepared asbestos in the case of fire brick caused a very marked diminution in the heat losses.

As regards the saving in heat losses with large furnaces, one experiment may be quoted. The total outside surface of the furnace exposed to the air amounted to 20 square meters; the furnace was heated by means of a resistor, and it was possible to make determinations of the heat losses at various temperatures. It was found that at 1100° C. the loss amounted to 38 kilowatts. Observation showed that there was considerable difference in the temperatures of the outside walls. About 4 square

meters of those parts of the outside of the furnace which were hottest were covered with the "insulating building brick" referred to in the table above and another determination of the heat losses made, which showed that these now amounted to 32 kilowatts.

DISCUSSION.

PROF. J. W. RICHARDS: If two furnaces are taken which have two different chemical reactions occurring within them, one absorbing twice as much energy as the other, it is possible to have the electrical energy converted into latent chemical energy at a much higher rate in that furnace where the greater endothermic reaction is taking place. It is of importance to keep this in mind when comparing the heat insulation of furnaces. The loss of heat from furnace walls by convection is very important. In some recent experience a loss of heat proportional to the velocity of the air rather than the square root of the velocity has been indicated. As regards insulating materials, I have seen in Europe bricks of aluminum nitride used. At temperatures around 1600° to 1800° these bricks have low electrical conductivity and are better heat insulators than any other materials so far tried.

A paper presented at a Joint Meeting of the American Electrochemical Society, the American Institute of Mining Engineers and Sections "Electrochemistry" and "Metallurgy" of the Eighth International Congress of Applied Chemistry, in New York City, September 7, 1912. Professor W. Lash Miller in the Chair.

ELECTRIC INDUCTION AND RESISTANCE FURNACES FOR STEEL

By C. H. Vom Baur.

Electric steel furnaces of the induction type have been in operation for over a decade, using single-phase current. Lately, furnaces of improved design have been operated directly from two-phase and also from three-phase current without any previous transformation into the simpler single-phase.

I wish to lay before you a few recently determined facts concerning the action of the rotating field which is present in polyphase induction furnaces.

This rotating field is the short-circuited secondary, or the molten metal; and in the two-ton size Roechling-Rodenhauser furnace this rotating field of molten metal wore out the lining too rapidly at certain places in the hearth. Oddly enough, when this same style of furnace was made a little larger, in a three-ton size, the rotating field did not manifest itself sufficiently to have any deleterious effect on the lining, owing no doubt to the widening of the hearth. The lining lasts as long in this case as in a single-phase furnace of equal size, for as many as four to five hundred heats have been taken from one lining when using hot charges, and about half as many heats when charging cold material. In order, however, to simplify the polyphase furnace hearth, and consequently lengthen the durability of the lining, it was deemed best to construct the furnace on the two-phase principle. This furnace construction has two transformer cores protruding through the bath, instead of three, as with the three-phase furnace. This two-phase construction employs the well-known figure-eight hearth, which, in addition to being simpler from both an electrical and metallurgical standpoint, is also more efficient thermally, as the radiation losses are less. Metallurgically the furnace is better and easier to operate,

as the hearth is wider and shorter compared to the corresponding single-phase size having the same shaped hearth. This makes the rabbling-off of slag easier than with the single-phase furnace, and, compared with the three-phase style furnace, this rabbling is also more convenient, as the slag is removed from doors which are in a straight line with the spout.

This two-phase type of construction is also more simple compared to the three-phase type, as only two coils are wound about the transformer cores instead of three. When three-phase current must be used, it is transformed in the furnace itself to two-phase, without employing auxiliary transformers having the well-known Scott connection. The heat regulation of the furnace is then accomplished by regulating the three-phase incoming current by means of a simple and inexpensive three-phase induction regulator. This improvement will also decrease the installation cost. I am glad to say that all Roechling-Rodenhauser and improved type induction furnaces will be built in this form.

I now wish to lay before you a new metallurgical fact concerning steel at a very high temperature, such as has been attained in the induction furnace. It is a high-temperature phenomenon which might be called a new critical point of iron.

A test was carried on in an eight-ton induction furnace having enough electrical power behind it for a fifteen-ton furnace of this type. The full capacity of the alternator was used for the test, and, as there was power to spare, the charge was greatly overheated. In fact, the temperature obtained was so high that the magnesite lining was completely fused even below the slag line, which indicates that the temperature must have been at least 2400° to 2600° C.

Common steel, as is well known, has a critical point at a temperature of about 760° C., and when arriving at this point it seemingly does not rise in temperature so rapidly, whereas when the temperature reaches about 810° C. a sudden and rapid rise in the temperature of the steel takes place. The same thing seems to be repeated at the higher temperature alluded to, and another critical point seems to be reached. The metallurgists present at this test stated that when a temperature of about 2350° C. was obtained, the steel became thick and viscous. However, after the temperature had risen some 200° higher it again became

liquid and was then poured into the ladle. There it was naturally cooled down somewhat, and became again thick and viscous to such an extent that it was impossible to empty the ladle into the ingot moulds. A heavy rod of cold steel about eight feet long and two inches in diameter was then put into the ladle, by means of which the steel was cooled down below the critical point, whereupon it suddenly became as liquid as water and could be easily emptied into the moulds. The ordinary tests showed that the steel was of the usual good quality, but no other tests were made on it to determine whether or not this extraordinary heating had had any other effect upon the metal.

I regret to say that the latest developments and improvements made in induction furnaces this year in Germany, which I expected to lay before the congress at this time, have been delayed in reaching me, but in closing I may add that the Roechling-Rodenhauser induction furnaces and their improved types will shortly be built in sixteen and twenty-ton sizes, both here and abroad.

DISCUSSION.

Mr. S. M. Rodgers: I did not expect to be called upon to talk about electric steel, as I have not been keeping closely in touch with the operations of this furnace for some time. During the past eighteen months we have made a considerable tonnage of steel, varying in composition, which has been used for many different purposes, such as rope wire, music wire, hat wire, card wire, and many other grades of wire, running high in carbon, low in sulphur and phosphorus and about the usual percentage of manganese and silicon.

In one of the papers just read reference was made to electric steel having a greater density than open-hearth steel of like composition. Our experience in this respect would indicate that this is true, although we have made no special tests to confirm our observations. A much larger percentage of the electric steel manufactured at our Worcester Plant was made on the basic hearth than on the acid, although comparative tests were very carefully made with acid open-hearth by manufacturing the same

grades and sizes of wire from all three kinds of steel and subjecting the finished wire to the same physical tests. In many of these tests the three grades of steel were carried through the processes at the same time and under as nearly identical conditions as possible, thus eliminating to a large degree such differences as might be due to slight variations in treatment. Where it has been practicable, life or service tests were given the finished product, *e. g.*, rope wire would be fabricated into rope and tested as nearly as possible under conditions of service practically to complete destruction and the results tabulated. There was no marked difference in the physical qualities of the finished wires before fabrication, and the average results in the service tests showed the acid open-hearth steel to be the best, although the difference was not very great. In the drawing operations the electric steel always seemed to harden more than the acid open-hearth and was generally a little more brittle and not so tough. For music wire electrical steel was not very satisfactory because we were never able to produce a grade that would meet the specifications in swaging and eyeing, because the failure to meet these tests indicates serious irregularities in physical composition which are not easy to overcome in the process of manufacture. While we have made some fairly satisfactory piano wire out of electric steel, the percentage was small and the cost high. Piano makers are not willing to take any risks in using wire which has not been fully tested.

In manufacturing acid open-hearth steel for high-grade wires great care is used in selecting the charge, while this is not true to the same degree in making electrical steel, although the difference in quality cannot certainly be traced to the difference in the charges.

In making low carbon electric steel, problems of greater difficulty were involved. To properly deoxidize the bath of low carbon steel, both time and expense are required, which makes it difficult to compete with well-made basic open-hearth steel. I may say, however, that we have not done a great deal of experimenting on the low carbon steel.

Mr. William Brady: Mr. Chairman, I do not know that I can add anything to what has been said. This able paper

has covered the question thoroughly—I recognize some things in it—and Mr. Rodgers has also covered the subject of electric wire. As you know, we make our electric steel from the blown metal, and the product has been put principally into rails and castings. The steel is now being subjected to the crucial test of use, and so far reports are very encouraging in regard to the properties of electric steel.

Mr. F. N. Speller: So far we have not used electric steel to any extent except experimentally. As you are probably aware, there are two lines of tubular product made in the United States; seamless and welded, which require somewhat different grades of steel. The electric steel is much better adapted to the seamless product than the welded. Extreme purity is apparently not consistent with good welding quality, as experience with very pure steel, made in the open-hearth furnace, and electric steel have shown. On the other hand, these steels are better adapted than the ordinary product to the severe manipulation which the metal must go through in making a seamless tube.

C. H. Vom Baur: I would just like to say that electric steel rails have also been laid on the Prussian State Railways, and have been in use there for the past four years, and also have shown no breakages. All these were made in the electric induction furnace.

Dr. R. Amberg: I do not know whether I fully understood the remarks of Mr. Vom Baur concerning the new recalescent point in liquid steel. There are quite a number of recalescent points in solid material. There is very little known, however, about recalescent points above the melting point. Maybe Mr. Vom Baur can tell us some more interesting data on that subject.

Mr. Vom Baur: Unfortunately, I could only say what I have already said, but if it will clarify the situation I could go over the point again. It is only this—that when the metal reached this point, 2350°, the steel became thick and viscous. When it reached to 2500° it became liquid again. Then it was poured into the ladle and cooled to get it down again from that point, this was done by swirling a large rod around in the metal. It was then cooled down, became liquid as water, and was poured.

It was blown basic Bessemer metal, then put in the electric furnace.

PRESIDENT MILLER: The steel seems to behave very much like sulphur, as you have pointed out. Am I right in understanding that immediately on cooling below a certain temperature range the viscous liquid became fluid—that the change took place quickly?

MR. VOM BAUR: Very quickly.

PROF. J. W. RICHARDS: The difficulty in welding electric steel is undoubtedly due to the almost total absence of included slag. The more included slag there is in iron the easier it welds. Wrought iron which contains the most intermingled slag welds the easiest. An induction furnace near Stavanger, Norway, is used for refining steel scrap previously melted in an open-hearth furnace. The work shows that it is cheaper to melt with fuel at $4.00 per ton than with electricity at $8.00 per horse-power year, but for the refining the electric power is cheaper and far more efficient.

DR. R. AMBERG (*Communicated*): H. C. Greenwood found the boiling point of iron at 2450°. As his experiments were carried out on a laboratory scale with all the accuracy possible under the circumstances of extreme temperatures, while Mr. Vom Baur, as I understand, made an occasional observation on 0.08 percent carbon steel in an 8-ton furnace during its run, it might be worth while to revise his temperature determinations and check the phenomena.

A paper presented at a Joint Meeting of the American Electrochemical Society, the American Institute of Mining Engineers and Sections "Electrochemistry" and "Metallurgy" of the Eighth International Congress of Applied Chemistry in New York City, September 7, 1912. Professor W. Lash Miller in the Chair.

ELECTRIC HEATING AND THE REMOVAL OF PHOSPHORUS FROM IRON

By Albert E. Greene.

Processes for the removal of phosphorus from iron or steel are steadily assuming greater importance in view of the abundance of high-phosphorus iron ore and the diminishing supply of pure ore. In the present processes of removing phosphorus by the Basic Open Hearth or Basic Bessemer, or even by electric processes, complete control over the metallurgical conditions is either impossible or has not yet been realized. The removal of phosphorus has so long been accomplished along certain well-defined lines, that when the electric furnace made its appearance metallurgists stuck to the same old reactions used in the older processes and failed to appreciate and take advantage of the new forces at their disposal. It is one object of this paper to set forth more clearly the metallurgical reactions by which phosphorus can be removed from iron and to show the necessity of controlling the conditions and particularly the temperature by means other than combustion in the furnace chamber.

Invariably, the commercial removal of phosphorus has been accomplished by oxidation. The reactions involved in oxidation of phosphorus in general consist first of the formation of P_2O_5, and second, the combination of this oxide with lime, forming calcium phosphate, which latter is held in a slag high in oxide of iron. In the present-used processes, the phosphorus is never removed without the assistance or presence of considerable quantities of oxide of iron. The oxygen for removal of phosphorus in the basic open hearth process comes largely through the medium of oxide of iron and furnace gases, but not from lime, and the lime itself cannot prevent the reduction of phosphorus back into the metal out of slags from which oxide of the iron is largely

reduced, and likewise in the Basic Bessemer process, although here the oxygen comes originally from air, yet oxide of iron formed in the blow is the essential carrier of oxygen.

Among the more important metallurgical conditions which control the reactions of phosphorus are the temperature, the presence of oxidizing agents or reducing agents, or both, and the intensity of the resulting oxidizing or reducing conditions, or, in other words, the equilibrium conditions governing the reactions involving oxygen; the influence of slags, including the influence of oxides therein having affinity for oxide of phosphorus, or other phosphorus compounds, the solubility in the slag of such phosphorus compounds, the presence of oxide of like chemical nature to phosphorus oxide and tending to displace it; and the affinity of the reduced metal for phosphorus. In processes where the heat is supplied by combustion it is not possible to maintain complete control over all the above conditions. In the open-hearth furnace the temperature is maintained by combustion of gas in the furnace chamber, and the atmosphere is oxidizing to a greater or less extent. Any control over the reducing conditions in an open-hearth furnace must therefore come from reducing agents in the metal, and very limited control, if any, can be had over the action of agents such as silicon or dissolved carbon. Since oxide of iron can not be kept from forming in the slag under influence of the furnace atmosphere, it is apparent that the silicon or carbon in the metal are the agents which must be relied upon to prevent such oxidation.

To hold the strongly-acid oxide of phosphorus in the slag requires a fluxing agent having strong affinity for phosphorus and which is strongly basic in chemical nature, like lime. Calcium phosphate is not at all difficult to reduce, however, at an elevated temperature and with strong reducing agents, and either silicon or carbon is capable of reducing it. This statement holds true even though the carbon or silicon be dissolved in iron, although the intensity of the reducing action is then less, possibly owing to the "pulling action" of the iron itself on these reducing elements. The temperature may, of course, greatly influence the action on the slag of these reducing agents contained in the metal, and may so change their affinity for oxygen as to prevent reduction of certain oxides in the charge, as is the case with

carbon and phosphorus. In an open-hearth furnace calcium phosphate will be reduced from the slag back into the metal when the conditions of equilibrium between the oxides of iron in the slag and the reducing agents in the metal are such as to reduce the amount of iron-oxide below a certain limit. Silicon is such a strong reducing agent that practically always, except in certain cases to be noted later, it must be oxidized out of the metal before the phosphorus is attacked. If present in the bath it reacts with any oxide of phosphorus present and reduces it. The presence of large amounts of silica in the slag or lining of the vessel is ordinarily detrimental to removal of phosphorus.

The influence of carbon, the other important reducing agent in the metal, is largely dependent on the temperature, its affinity for oxygen being less than that of phosphorus at low temperatures, and greater at temperatures above about 1450° C. Thus, at low temperatures, carbon dissolved in the iron is not a strong enough reducing agent to reduce calcium phosphate held in a slag high in oxide of iron, but at higher temperatures it is. Thus, either by means of silicon or by means of carbon contained in the metal, or, of course, by solid carbon, the oxide of iron in the slag may be readily reduced, and when such reduction proceeds far enough calcium phosphate is also reduced and the phosphorus goes back into the metal.

The fact that at low temperatures phosphorus is more easy to oxidize out of the metal than carbon is the basis of several modifications of the open-hearth process, such as the Krupp washing process, the Bertrand-Thiel process, etc. The slight differences in these processes, such as the heating up of ore, lime, and pig iron together, or the preliminary heating of the ore and lime and subsequent use of molten pig iron, do not change to any great extent the final result as to the method of removing phosphorus. The manner of carrying out this oxidation of phosphorus determines the degree of activity and frothiness of the slag, but essentially the reaction is the formation of calcium phosphate in the presence of considerable oxide of iron.

In the operation of the Basic Bessemer process, the chemical reactions involved in the separation of phosphorus are in reality practically the same as those in the open-hearth process. In the Bessemer process, temperature is maintained by combustion as in

the open hearth, the combustible materials being the silicon, phosphorus, iron, carbon, etc., of the charge, and also these are burned with an excess of oxygen to produce the necessary heat. Oxidation of the phosphorus results from oxygen of air primarily, but oxide of iron formed from the air acts as a carrier of oxygen, just as in the open-hearth process the slag serves as a carrier of oxygen from the furnace gases.

A large proportion of the heat evolved in the Basic Bessemer process results from the oxidation of phosphorus, but it has been found that a certain proportion of silicon is necessary in the pig iron to produce the requisite final temperature. Silicon is oxidized first, together with iron, and thereby the temperature of the bath is raised above that known as the critical temperature between carbon and phosphorus, and above this critical temperature the phosphorus is not removed appreciably until after both the silicon and the carbon are largely oxidized out. In certain cases with low silicon, oxidation of phosphorus takes place from the early part of the blow simultaneously with that of carbon. This is what would be expected if the temperature be held at about the critical point, since at this temperature the oxidation of carbon and the formation of calcium phosphate take place with equal readiness.

An interesting example of the effect of metallic reducing agents in connection with the Basic Bessemer process is the rephosphorization of the metal on the addition of spiegel. The spiegel enters the metal at a high temperature and through a slag containing considerable quantities of calcium phosphate. At an elevated temperature, both silicon and manganese are easier to oxidize than phosphorus, and these two elements tend to reduce the phosphorus from the slag back into the metal. From recent experiments of the writer, it has been found that at a low temperature phosphorus, on the contrary, is more easily oxidizable than manganese in the presence of lime and can be separated as calcium phosphate without oxidation of manganese. The reactions involved will be discussed more fully later.

On comparison of the conditions in the Bessemer and Open Hearth process, it is seen that the controlling factors in the separation of phosphorus are almost identical. Lime is, of course, necessary to hold the phosphorus in the slag. Combustion is the

source of heat and iron-oxide is always present and usually in large amounts; silicon oxidizes before phosphorus, and the oxidation of carbon before or after phosphorus is determined by the temperature. Lack of complete control over the reactions resulting from producing the requisite temperature by combustion in the furnace chamber, and necessitating loss of iron as oxide in the phosphate slag, is the very feature which electric heating can correct.

The electric furnace has been found well adapted to removing phosphorus by oxidation in the old way, but not commercially, and on careful consideration it is difficult to see how it could do so commercially in competition with the open hearth. The process of removal of phosphorus in the Heroult furnace, for example, as practiced by the United States Steel Corporation, has been to charge blown steel into the furnace and melt on top of it a slag of lime and iron oxide. The reactions are identical with those in a basic open hearth. And in spite of the fact that the temperature can be maintained high, the removal of phosphorus in a large furnace takes anywhere from twenty minutes to an hour and a half, according to the amount of phosphorus removed. After the phosphorus is separated in a slag high in oxide of iron, that slag has to be removed in order that the bad effects of the oxides contained therein on the steel may be remedied. It is certainly difficult to see wherein lies the advantage of using costly electrical energy, electrodes, etc., to do the same thing that is done with cheaper fuel heating in a basic open hearth. And this is gradually becoming realized. After removing this first slag, it is replaced by a reducing slag to remove the oxygen from the metal. Here metallurgists have gone to the other extreme; they have aimed at and obtained the strongest reducing conditions possible by use of solid carbon and high temperatures. They have used as a measure of the intensity of such reducing conditions the formation of carbide in the slag. And these conditions are such as will readily reduce phosphorus compounds in the slag.

One method of avoiding two slags was proposed and tried out. It consisted in the use of a solid reducing agent, such as fine coke, added to the oxidizing slag after the phosphorus had been taken up by that slag. The object of this was to reduce the iron-

oxide of the slag and leave the phosphorus as calcium phosphide. The results of the tests on this process indicated that the use of a solid reducing agent at the elevated temperatures necessary in a steel furnace not only reduces the iron, but also the phosphorus, and the latter goes back into the metal. No other result could have been expected. The explanation of the above reaction is simply that solid carbon has a stronger affinity for oxygen than has phosphorus at the temperature of molten steel in an electric furnace, even though the phosphorus be combined with lime as calcium phosphate. In other words, the reducing conditions acting on the slag are so strongly reducing that phosphorus goes back into the metal.

High phosphorus iron-ore has been partially reduced in the presence of lime without practically any of the phosphorus entering the metal, the phosphorus being retained in a slag very high in oxide of iron. Such reduction of iron and separation from phosphorus has been carried out in an electric furnace by using insufficient carbon to completely reduce the ore, since solid carbon, if present, will of course reduce the calcium and iron phosphates at the elevated temperature maintained. The action here of solid carbon is similar to that in a blast furnace, where the presence of an excess of solid carbon causes reduction of oxide of phosphorus and phosphorus is found in the metal. In an electric ore reduction furnace, even with a basic lining, excess of coke will produce the same result and the presence of lime does not overcome this effect. On the other hand, in an electric reduction furnace, when the carbon-reducing agent is limited, the phosphorus does exactly what it does in an open hearth: slags with iron-oxide as iron phosphate, and combines with lime to form calcium phosphate after the carbon is used up by combination with oxygen of the ore. The above facts show why it is not possible to reduce iron from the first slag in the Heroult steel refining furnace by use of coke without reducing phosphorus back into the metal.

It is a fact that at an elevated temperature oxide of iron is more easily reduced than calcium phosphate, and it is evident that if the proper intensity of reducing conditions be maintained at the elevated temperature, oxide of iron may be completely reduced without reduction of calcium phosphate. Such condi-

tions are obtainable by use of a gaseous reducing agent, such as ordinary producer gas, meanwhile maintaining the temperature electrically.

The various reactions of phosphorus associated with iron may be summarized as follows:

1. At temperatures under 1450° C., phosphorus in pig iron has greater affinity for oxygen than has the carbon in the pig iron, but less affinity for oxygen than solid carbon in the presence of pig iron.

2. At temperatures above 1450° C., the affinity of the carbon dissolved in iron for oxygen becomes greater than the affinity of phosphorus in the iron, and the dissolved carbon can reduce calcium phosphate in the slag; of course, solid carbon can do this also.

3. Phosphorus oxidizes in presence of lime and iron-oxide to calcium phosphate, in absence of silicon or solid carbon.

4. Silicon reduces calcium phosphate nearly always, but there may be a range of temperature under 1450° where phosphorus oxidizes to calcium phosphate more easily than silicon to calcium silicate.

5. Solid carbon will reduce calcium phosphate contained in a slag or bath of iron and phosphorus will go into the metal.

6. Calcium phosphate can form without oxidation of iron in presence of carbon dissolved in pig iron at low temperature.

7. Calcium phosphate can form without oxidation of iron in absence of carbon and silicon at high temperatures; *i. e.*, above 1450° C.

8. Oxide of iron can be reduced without reduction of calcium phosphate contained in the same slag.

9. Solid carbon is a stronger reducing agent than carbon dissolved in the iron, probably because of the affinity of the metal for carbon.

It is apparent that in all of the present processes the complete control of at least one important factor is either lacking or has not been utilized. In the open-hearth process it is the control of the reducing conditions that is limited, and likewise in the Bessemer process; but in this latter process, the control is further

limited by the necessity of raising the temperature by oxidation of elements in the charge itself. In the electric furnace, however, where heat can be produced independently of combustion or chemical reaction, this important factor—namely, intensity of reducing conditions—can be controlled at will and with ease. Up to the present time this fact appears not to have been appreciated by metallurgists, judging by present methods. It is in the complete control of the reducing conditions that important possibilities of electric heating lie, and as this fact becomes more generally recognized and used it is probable that some method will be devised for measuring the intensity of reducing conditions or equilibrium conditions. Since the intensity of reducing conditions is the reverse of the intensity of the oxidizing conditions, the term "oxygen pressure" may find use as a measure of them.

Among the reactions made possible by control of the reducing conditions and temperature simultaneously, is the reduction of oxide of iron from a slag containing calcium phosphate without reduction of the phosphorus contained therein. Naturally, the origin of the phosphorus containing slag or charge is immaterial; it may be raw ore containing phosphorus, or it may be a slag in which some of the original oxide of iron served to provide the oxygen for combination with phosphorus, the oxide of phosphorus subsequently combining with lime to form phosphate. Or the reducing conditions may be so controlling as merely to prevent oxidation of iron, which, at the same time, causes phosphorus to oxidize and combine with lime.

In the writer's experiments along this line it has been found that at temperatures below about 1400° the phosphorus was easier to oxidize than carbon from pig iron. And it was found that the phosphorus could be oxidized in the presence of lime without any resultant oxidation of iron and with practically no oxidation of carbon; that phosphorus could be oxidized in the presence of lime without oxidation of manganese; and a very interesting further observation was made, namely, that at certain temperatures between the melting point of pig iron and about 1350° C., phosphorus oxidized in certain cases in the presence of lime without any appreciable oxidation of silicon. This would indicate a reversal of oxygen affinity of these elements—phosphorus and silicon in pig iron in the presence of lime.

A fusible slag results from proper proportions of acid and basic radicals. It has been found that the silica content in the slag may be as high as 30 per cent. without apparently hindering the removal of phosphorus. Phosphorus was separated in slags containing this amount of silica and yet practically no iron oxide was present in that slag. This points to the possibility of a low-melting-point slag for holding phosphorus.

The reduction of oxide of iron from a charge or slag containing phosphorus as calcium phosphate, without reduction of the latter, requires essentially the same control of the conditions as does the selective oxidation of phosphorus in presence of lime, forming calcium phosphate without oxidation of iron. Electric heating is the only practical way of accomplishing such control.

It is not to be doubted that metallurgists will very soon appreciate the distinction between various degrees of oxidation and reduction, where they have not already done so, since in so many cases undesired elements can be separated from metals by oxidation of the impurity and reduction of the metal. When this becomes generally appreciated it is prophesied that electric heating will come into use to an extent that is now hardly thought possible.

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THE FUNCTION OF SLAG IN ELECTRIC STEEL REFINING

By Richard Amberg.

While the old time melter was satisfied to bring his metal out in the desired condition and therefore took care to have the slag liquid enough, the importance of a thoro knowledge of the slag is at present recognized in all up-to-date melting shops. Formerly, slag or cinder was considered a necessary evil, accumulating in some mysterious way wherever a man was striving to produce a clean metal. Nowadays we are deliberately aiming at a well-defined slag which varies with the nature of processes applied and products wanted.

In steel making we need, in general, slag for two main purposes, viz.: for refining and for protecting the metal. To refine metal, essentially oxidizing processes are required, while to protect the metal we need a reducing or, still better, a neutral atmosphere. Although an absolutely neutral condition between steel, on one side, and the containing vessel and the slag, on the other, is an imaginary conception, the various furnaces in use for the production of liquid steel may be arranged with respect to the attainment of this ideal in about the following order of merit: converter, open-hearth, crucible, and electric furnace.

In dealing with our subject we will find it convenient to avail ourselves of the terms of physical chemistry, which yield a simple conception of the matter and an expedient way of expression.

Slag and metal in general are not miscible with each other, and we will therefore call them the two "immiscible phases," though there are certain compounds which dissolve in both phases under conditions to be considered later on. Reactions between chemical compounds can take place in either phase; they are independent of the reaction in the other phase as long as the product of the reaction remains in its own phase and does not

cross the boundary surface. A reaction of this kind, where the original and the final product are entirely in one and the same phase, is a homogeneous reaction. If the other phase takes part by either supplying or absorbing substances, the reaction is heterogeneous. The homogeneous reaction is governed by the laws of homogeneous chemical equilibrium or mass action; it occurs uniformly throughout the entire phase.

Since, according to van't Hoff, at low temperatures an increasing of 10° C. doubles the reaction velocity, it will in most cases be infinitely high at the temperatures of the steel bath. The heterogeneous reaction, however, must take place at the contact surface of the two phases. Its speed depends greatly on the velocity with which the substances participating in the reaction are brought to the contact surface, and carried away from it. That is, it depends greatly on diffusion and mechanical convection.

Every condition which makes the slag less viscous and more mobile, facilitates, therefore, a heterogeneous reaction. Further, the greater the area of the contact surface between the two phases, the more is the heterogeneous reaction facilitated.

Some time ago[1] the author pointed out briefly these facts, which are discussed more in detail in the present paper.

The above considerations will hold good for many kinds of metallurgical operations. When applying them to a practical case we have to bear in mind that slag and metal are very seldom separated by a sharp surface; small particles of slag are hanging through the surface of the metal, are cut off and scattered through the bath, and little balls of steel are oftentimes found mixed within the slag. Considering a steel furnace in operation, we have to deal with at least four phases; *viz.:* the slag and the metal, as the two liquid phases, the atmosphere above the bath, and one or more solids in the hearth of the furnace. The solid phases, however, can be disregarded entirely for the purpose of this paper, while the gas phase will occasionally have to be taken into account.

The function of the slag in an electric steel furnace depends on the kind of work which the furnace is performing, that is, the particular process which is carried out, and in one and the

[1] Met. and Chem. Eng., 7, 115 (1909); also Stahl und Eisen, 1909, No. 5.

same process the function of the slag depends on the stage which the operation has reached at that time.

At places, where cheap power is available, electric steel melting begins with the most widely known open-hearth process—melting pig and scrap. It is also possible to start with steel scrap without any pig iron, although this is not an advisable practice, since it is hard on the lining. Assuming a basic-lined bottom and hearth heated by one or more electric arcs, the charge melts down, slag is formed by lime, silica, and iron-oxide in the form of ore or scale, and the refining by oxidation takes place in the form of heterogeneous reactions of different kinds. After the

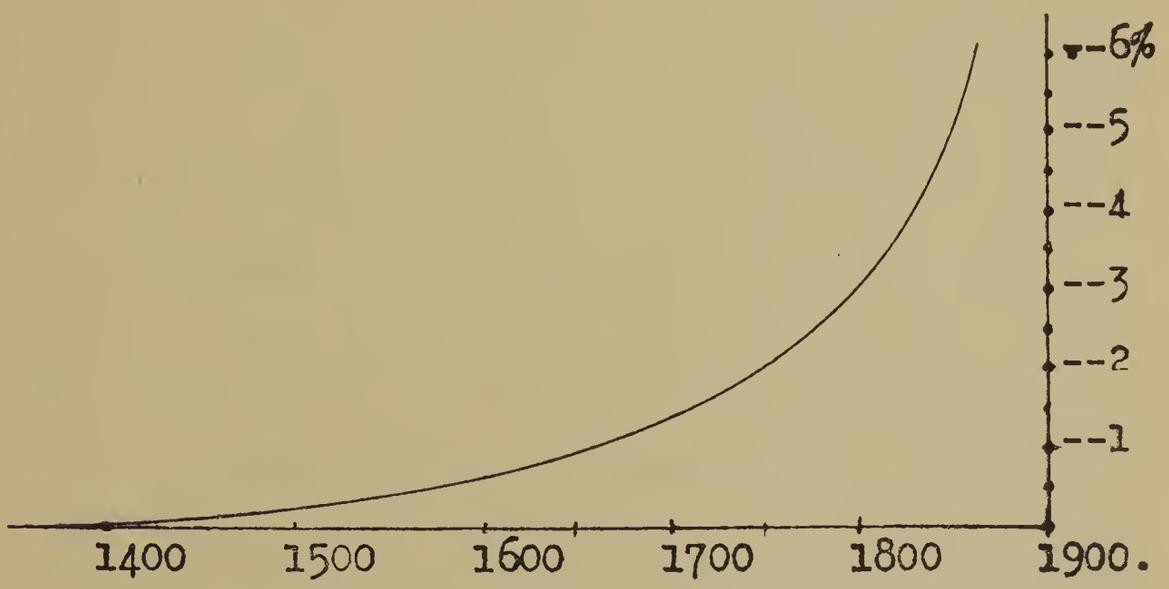


FIG. 1.

ferric oxide dissolved in the slag has been reduced to ferrous oxide, it partly acts directly on those parts of the metallic solution which come in immediate contact with it, and partly dissolves in the metal according to temperatures and coefficient of division of FeO between the two phases. If the slag is saturated with FeO, the latter can assume its full concentration in the metal bath according to the solubility curve given in 1906 by Prof. Eichoff. Its action here on manganese and the metalloids is much the same as in the open-hearth, and needs no discussion at this time. It can be more energetic, however, if the operator avails himself of the effect of a higher temperature, which is a special feature of the electric furnace, and, as Fig. 1 shows, of a higher concentration of FeO.

There is one essential difference from the reaction in an open-hearth slag. In a well-built electric furnace, practically all the oxygen required has to be supplied in solid oxide form, while the open-hearth has an unlimited supply of oxygen by opening its air inlets wide enough to have an excess of oxygen in its gases, from which the slag continuously and automatically replaces the amounts transferred to the steel. A poorly constructed electric furnace, which the author once saw, produced such a tremendous draft of air through its doors that it needed almost as little ore as an open-hearth furnace.

At this period of oxidation the basic slags of an arc furnace and of an induction furnace show a material difference; the dephosphorization, being a process which reaches its maximum velocity at a temperature somewhat below the melting point of soft iron, is accomplished more quickly in the comparatively colder slag of the induction furnace than under the higher heat of the arc. The technical significance of this fact, however, is small at the present time, since the general and indeed reasonable tendency is to do as much of the refining work as possible in the open-hearth furnace and reserve for the electric furnace merely those finishing operations for which it is especially fitted, and which can not be performed in the open-hearth.

In view of the above described conditions, the analysis of the slag during this period does not offer any particular interest in comparison with open-hearth slag. CaO will run in the neighborhood of 40 percent, sometimes 5 to 8 percent lower, iron and manganese oxides 26 to 29 percent together, and the silica will vary with the silicon of the charge, and the additions. P_2O_5 may run up to any amount in crude open-hearth work, yet, as a rule, the slags have been skimmed when it reached something like 4 percent. As manganese ore, even at this stage, helps desulphurization, it seems to act locally, perhaps near the electrodes only, in a manner which will be discussed later on.

After this oxidation has been carried on far enough, and the slag removed, or after dephosphorized metal has been transferred from another furnace to the electric furnace (which practice is the rule in the present centers of the steel industry), the metal will be de-oxidized in the furnace. This involves a slag process which none of the other furnaces can perform. Carbon is the

chief de-oxidizing agent, and is bound to act in both phases. Experience has shown that this element alone can complete the de-oxidation, but it is not practical commercially to do this, as it takes too long a time. While the action of carbon on oxides in the homogeneous metal phase probably goes on with sufficient velocity, yet its action on the oxides of the slag, being a heterogeneous reaction, is pretty slow. We know that glass can be colored by small quantities of carbon, but we have not found that any amount of carbon worth while could exist dissolved in the slag phase. Furthermore, when the metal will be freed from the compounds which are soluble in both phases, these compounds will have the tendency to diffuse back from the slag into the metal as soon as favorable chemical and thermal conditions arise.

Phosphorus may be mentioned as an example of this statement. An iron-phosphide exists in the metallic solution; by oxidation, transfer to the other phase, and neutralization with CaO, it forms calcium phosphate. When finishing a basic open-hearth heat the amount of oxygen in the slag decreases gradually and can reach a point where the other sources of oxygen are so much exhausted that the phosphate begins to be reduced by iron or manganese and the phosphorus re-enters the bath—one of the dangers which the skilled melter knows how to avoid. Here the electric heating, as described in the patents of Humbert, offers the possibility of heating the slag with the addition of carbon in a reducing atmosphere so quickly that it forms a considerably higher endothermic compound, probably Ca_3P_2, which is not reabsorbed by the steel phase; hence the opportunity to dephosphorize without skimming the slag. How sensitive this reaction is with respect to temperature, is shown by the fact that without very accurate control of the temperature a re-phosphorization of the metal has been found.

Since in the reducing atmosphere, when carried on far enough, the partial pressure of oxygen is very low, the oxygen can be removed to a considerable extent from both phases without disturbing the equilibrium at the contact surface, while the opposite would be the case with an open-hearth furnace. In fact, the amount of FeO present in the final slag is easily brought down in every-day practice to between 1 percent and 0.5 percent,

and, with a little attention, considerably lower. The reaction by which this is performed is a true heterogeneous one and consequently does not come to an equilibrium in the original phase. FeO as a base of the silicates or as dissolved in the slag is freed from oxygen, and the metal joins the other phase. Manganese is practically removed from the slag in a similar way. Even silicon is partly reduced, when both the basicity of the slag and the temperature are high enough.

The desulphurization has been the subject of many experiments and discussions. No doubt there are three phases, the atmosphere and the two liquids, connected with this phenomenon. In the oxidizing period, where sulphur is being removed only to a small extent in the open-hearth, the electric furnace is much more efficient in this respect, especially when manganese ore is used. It is likely that a good bit of the sulphur forms SO_2 and disappears with the gases; as the partial pressure of O and of SO_2 in the atmosphere of the electric furnace is smaller than in the open-hearth, the reaction takes place more easily. This is the reason why, as previously mentioned, the electric furnace in all other respects is less good an instrument for oxidizing refining than the open-hearth.

In the reducing period a new desulphurizing action takes place, which the author formulated some time ago.[2]

At high temperatures of the arc furnace:

$$(1)\quad FeS + CaO + C = Fe + CaS + CO$$

At still higher temperatures, where the calcium carbide can be formed:

$$(2)\quad 2CaO + 3FeS + CaC_2 = 3Fe + 3CaS + 2CO$$

At the lower slag temperature of the induction furnace:

$$(3)\quad 2FeS + 2CaO + Si = 2Fe + 2CaS + SiO_2$$

A possible explanation is that FeS, distributed between slag and metal so as to produce equilibrium, takes part in one of these three reactions, new amounts diffuse from the metal into the slag, and so forth. The reaction requires a high temperature,

[2] Stahl und Eisen, 29, No. 5 (1909).

and even then takes much time. This must be considered in connection with the possibility of reversing all the above reactions by introducing small amounts of iron or manganese oxides:

$$CaS + FeO = FeS + CaO.$$

This equation occurs from left to right for comparatively small amounts of oxygen, while from right to left it is the underlying principle of the three reactions, 1 to 3.

In all the foregoing reactions, one feature deserves the most important consideration, that is, the high basicity of the slag; this, in turn, is made possible by the high temperature attainable, especially in the arc furnaces. The law of mass action, which is directly applicable to homogeneous reactions only, describes the effect of the high concentration of CaO. Whatever silicates and aluminates of iron and manganese, of nickel, chromium and other metals have been formed, they will be decomposed by its stronger base. This condition is also aimed at in the basic open-hearth. But it cannot be carried to the same extent as in the electric furnace, because over 55 percent of CaO would result in a rather dry viscous slag, and because the oxides thrown out of solution would not find a sufficient quantity of a proper reducing agent. When as low as 12 percent of FeO and of MnO have been reached, it is considered the lowest metal content. Occasionally, and in other than the pig and ore processes, lower figures may be observed.

The elements which in the present electric furnace practice take care of reducing these oxides are chiefly carbon in the arc furnace and silicon in the induction furnace. As already stated, the manganese is practically eliminated altogether, the FeO easily removed down to 0.5 percent FeO, nickel is reduced with great ease, chromium, tungsten, and vanadium, according to their inherent amount of free energy, with a larger consumption of power. Some of these elements are almost as liable to be oxidized by small quantities of oxygen as they are liable to be dissipated by volatilization, and in practical work some experience is required.

For explaining the mechanism of the reaction we avail ourselves of the advantage which was referred to in the introductory remarks, and which follows from our consideration of a system

of various phases, so that we do not need to make any assumptions as to what definite chemical compounds we have to deal with. It is usual, for instance, to consider open-hearth slags as solutions of the other constituents, such as CaO, $Ca_4P_2O_9$, Al_2O_3, FeS, CaS, etc., in iron and manganese silicates as solvents. In our case we are gradually decomposing the solvent and are reducing its concentration to zero. It would not be of any advantage to know how the different constituents are combined with each other, even if it were possible to answer at all such a question for molten solutions.[3]

It is of great importance, however, for the advancement of general metallurgical knowledge, to determine the melting point of the pure compounds and give the complete diagram of the melting point of their mutual solutions over as wide a range of concentrations as possible. Such work has been started in a splendid way by Vogt, Doelter and others, but we need a great deal more data to make them suitable for practical use. Some melting points are:

$FeSiO_3$	1050° C.
$MnSiO_3$	1150° C.
$CaSiO_3$	1220°-1125° C.
Mg_2SiO_4	1400° C.

Most of the open-hearth slags seem to keep in the neighborhood of the eutectic composition, *i. e.*, the one with the lowest melting point, in those cases where the compounds will form a eutectic. If one of the constituents is raised extraordinarily to a high concentration, the melting point as a rule goes up. Examples of this phenomenon are widely known, as, for instance, in the glass industry, the pure sodium and the pure potassium glasses as compared with the Na-K glasses with a melting point lower than each of the other two, mixtures of sodium and potassium carbonate, etc. Acid slags become viscous when the silica is artificially increased; basic slags increase their melting point with rising amounts of CaO, which can be easily raised over 75 percent under the influence of the arc without any fluorspar in the slag.

[3] Papers of James Hendrick (Journal Soc. Chem. Ind., 28, 775-778 (1909), *ibid.* 31, 520 f. (1911) and others, though very valuable for agricultural research, prove that chemical analysis alone can not solve the problems of the constitution of slags. Optical and thermal methods will have to be applied extensively.

As this latter mineral, which is used to a larger extent in American than in European practice, is a good solvent, it prevents the need of an excessive temperature. It further permits keeping the concentration in SiO_2 low. While 12 percent to 20 percent SiO_2 is often contained in the high calcium slags, they can also be built up almost entirely from calcium iron and manganese compounds with very low SiO_2. One such slag, for instance, analyzed in its main constituents: 39.10 percent CaO, 18.20 percent FeO, 13.80 percent MnO, and only 2.10 percent SiO_2. Such slags may be of increasing importance for special work.

The carbon thrown into the furnace and the carbon derived from the electrodes can produce several compounds. Prevalent among these are silicon carbide, calcium silicide and calcium carbide. This latter one seems to be the most persistent under operating conditions, and is recognized by the development of acetylene from cooled-off samples. It is only after this carbide has been formed to a certain extent that the de-oxidation of the charge can be relied upon as completed.

When this condition of the bath has been realized, the electric furnace represents the nearest approach to the ideal heterogeneous equilibrium between the different phases which has hitherto been accomplished in large scale metallurgy; converter and open-hearth are under the action of air and gas, the crucible metal takes up carbon and silicon, whilst in the electric furnace the action of the metal on the basic lining is almost *nil,* there is no exchange of elements between metal and slag. However, a small evaporation of ingredients of the slag takes place, and in this respect the induction furnace, with its cold slag, has a slight advantage over the arc furnace. Under certain working conditions of operation of an arc furnace, when it is thought advisable not to cover the electrode holes in the arch airtight, fumes can be seen passing through the small joint between electrode and roof brick. These fumes always leave a deposit on the cooler parts of the electrodes, in powder form. An analysis of them taken during the oxidizing period of a furnace showed, aside from minor quantities of other substances, SiO_2 4.50 percent, FeO 8.49 percent, Fe_2O_3 60.60 percent, CaO 8.10 percent. This composition allows the conclusion that after reducing the metallic oxides from the slag there will be a considerable volatilization of CaO and some less volatil-

ization of SiO_2, both being probably first volatilized as elements and then oxidized in contact with the atmosphere. Smaller lots of Si may, perhaps, take part in the desulphurization by forming SiS_2, a volatile compound which decomposes in contact with humid air or water.

In the foregoing we have discussed the points in which the chemical action of the slag of the electric furnace differs from the corresponding slags of other furnaces. What is to be said of the physical effect holds good in general, but it is important enough to be considered in connection with our former discussion. We have already seen that there is by no means an ideal two-dimensional surface between slag and metal, and that both phases penetrate each other to a considerable extent. This is due to the various operations which the charge has to undergo from the time of its melting. The boiling in the oxidizing period intermingles small particles and reverses their mutual position. Upsetting of the whole charge often takes place when pouring from one furnace into a transfer ladle, and from there into another furnace. Then, there are the effects of stirring, making additions, which have to drop through the slag into the metal, etc. One might think that the difference of specific gravities from 3 to 7.8 should produce a clear-cut separation of the two phases by gravity, but the fact is that the separation proceeds astonishingly slow, even at higher temperatures and with the more liquid state of the materials of the electric furnace. The prevailing picture that slag and metal behave like oil and water is only relatively true. The slag swims on the metal, but where small parts of the one are caught in larger masses of the other, they have to overcome an enormous friction; and the smaller a particle of slag is, the larger is its friction surface in proportion to its gravity, and the more time and effort will be required to overcome its adhesion to the glue-like iron walls which surround it on all sides. Following this up, there is every reason to believe that, in dividing the particles of slag finer and finer, a point will be reached where the rising and separation of the slag particles would take such a length of time that all commercial advantage would be lost. If stirring could be performed so as to agglomerate small particles into larger balls which would have a stronger tendency to rise, an important advantage would be

gained. As long as we are not able to do this, we have to do the best we can by keeping the finished charge quiet and at a sufficiently high temperature to allow it to settle. Hereafter proper precautions will have to be taken while teeming and pouring, that the painstaking results of refining be not reversed. But these matters are outside of the scope of the present paper.

This slow physical action may furnish a new explanation for the slow progress of the desulphurization as per equation No. 2. The microscope shows that silicious and sulphidic products are sometimes contained down to two-thirds, and even lower, from the top of an ingot. These non-metallic products appear as balls in the ingot structure, and are elongated into a cigar-like shape after rolling or forging the metal. Although their melting point is lower than that of steel, they have not succeeded in uniting with the bulk of the slag in proper time. Consequently there is a lack of material in the slag, and desulphurizing can only take place whenever new sulphides are supplied. As the slag of the electric furnace allows of holding the metal, the sulphur can be removed to any desired extent.

A few words, however, may be said on the conditions obtaining when the electric furnace is lined with more or less silicious materials. Probably as a result of the experiments of the late Thallner, the acid electric furnace has quite recently won some reputation. An acid lining requires acid slag to keep the hearth in good condition. This acid slag will be much the same as the slag of an open hearth, as long as the charge is treated with an excess of oxides and the heat not exaggerated; if necessary it can be made to contain a higher percentage of SiO_2 for the same reasons set forth for highly basic slags. The great difference from the basic electric furnace is, in this case, that all four phases are in lively reaction with each other, that conditions approaching a status of equilibrium can not be reached, and that the metal must be "caught" at a certain moment for teeming.

The solid and the metal phase react in this way, that carbon of the bath reduces Si from the hearth, the amount of Si present being regulated by a reaction between the two liquid phases, namely, by keeping a sufficient stock of oxides in the slag to hold the Si within the required limits. The slag will therefore be a thoroughly black one, particularly during the beginning of

the run. Thallner ascribes a specific beneficial effect to this exchange of silicon and to the low heat conductivity of the silica lining. Towards the finishing of the acid heat the color of the slag clears up, and its reduction finally reaches a point where the glassy masses become light gray and green colored. Sulphur will, as in the acid open-hearth, remain unaltered in quantity, while phosphorus may be slightly decreased by phosphoric acid being thrown out of solution by the stronger SiO_2 and then reduced to phosphide of iron. This has to be confirmed, however, and it remains to be explained how this reaction can take place. Nothing definite can be said about it at the present time.

It may be that some of the advantages of this method are due to the mechanical property of the slag agglomerating more easily than the basic slag particles to larger globules, which force their way up to combine with the bulk of the slag.

While dealing with a subject of such real interest as this one, I need hardly say that a complete discussion of every detail is impossible and would conflict with the commercial obligations of the author.

There are, however, so many points still open to discussion, and also open to scientific research, that the author will feel much gratified if this paper acts as a stimulus to further discussion and research.

DISCUSSION.

Prof. J. W. Richards: The International Congress for Testing Materials spent recently over an hour in the discussion of this question of the slag inclusions in steel. There were shown some magnificent photographs of the slag inclusions in steel. Prof. Heyn, of Berlin, made the statement that the prejudicial character of slag impurities in the metal was proportional to the fineness with which they were disseminated; that when they were segregated in small lumps they were far less prejudicial to the character of the metal than when very finely, even microscopically disseminated, and the influence of such small amounts of impurities as a few thousandths of a percent of Al_2O_3 caused by the oxidation of the aluminium used for the deoxidization of the

metal was shown by photographs of one-thousand magnification. Engineers are just beginning to recognize the great influence on the qualities of fine steel of these intermingled slag particles, or slag-forming materials, microscopically disseminated. Dr. Amberg's paper is an important contribution to this subject. This quality of the slag, its ability to clean out the small particles of slag-forming material from the metal, its unifying or scouring action, is something which is not properly appreciated in the metallurgy of steel, but in the next few years I am sure its importance will be recognized. At the present time we have practically only three ways of meeting this problem. One is to regulate the composition of the slag as completely as possible. A second is to hold the metal in the furnace. I remember seeing in Germany one of those large 25-ton Bessemers blown for about twenty minutes, then turned down, and the metal held in the converter another twenty minutes (as long as it could be held there before casting) in order to give a chance for this emulsion of slag and metal to separate. The output of that great Bessemer converter and of the costly machinery was cut down at least fifty percent, in order to allow this resting of the metal in the converter, practically for no other purpose, and the cost of doing so was exceedingly high. These observations have led me to think that the final solution of this problem will be the holding of the steel melted in the electric furnace, simply keeping it melted for half an hour or an hour without any other treatment than letting it rest and allowing the slag and slag-forming impurities to settle out. When we do this, we are getting close to the last step in the purification of the steel.

Mr. Sinding-Larsen: The reaction between the sulphur present and the iron ore added is perhaps reduction by double reaction:

$$3FeS + 2Fe^2O^3 = 7Fe + 3SO^2$$

I have proved that iron ore can be reduced by iron pyrites—a similar reaction—and a countryman of mine has patented this process of reduction.

Mr. S. M. Rodgers: With reference to the remarks that have been made about the inclusion of slag, I would like to say that we have conducted some experiments which tend to support the

statements which have been made, by holding metal in the furnace for a short period of time and also in the ladle as long a time as conditions would permit. By taking samples from the top, middle and bottom parts of the ingots thus made and making microscopic examinations we find that the period of time had some influence over the amount of slag included. However, we have not made a sufficient number of tests to see how much better steel so treated would be than the regular product, but it is reasonable to assume that the less slag there is included the better the steel will be, particularly for high-grade products. There are some objections to holding the steel in the furnace or ladle for any great length of time after the completion of the refining operation, such as added expense, increased space and facilities required, etc. However, such objections are negligible if high-grade products only are considered, but not so when applied to large tonnages of low-grade products, such as structural materials.

With reference to my previous remarks, I wish to say that perhaps I did not make my position clear. It is my personal opinion, based upon observations we have made, that electric steel is better adapted to the manufacture of rails than it is to wire products. Why our processes of wire making are better adapted to open-hearth steels than to electric we cannot say; neither can we say what improvement might be made in the quality of wire manufactured out of electric steel by changing the processes. To some extent, however, changes have been made in our drawing practice and heat treatment, but the results were no better than what were obtained with our regular processes.

These tests do not necessarily prove that electric steel cannot be drawn as successfully as open hearth; but with our present knowledge of wire drawing, open-hearth steel is preferable.

Prof. J. W. Richards: In regard to the added cost of simply keeping the steel melted, it is costly when done by holding it in the Bessemer converter. The cost of holding the metal in an electric furnace without any treatment, simply keeping it melted, without any labor put on it, will be from twenty-five to fifty cents a ton, according to the cost of power. With this added twenty-five or fifty cents a ton, the steel can be given that

added freedom from intermingled slag which, while it may not show in rails, will show in steel used for severe service.

MR. E. R. TAYLOR: It seems to me that some experience in handling pig iron, which the American Steel and Wire Company have done for many years in Cleveland at their plant, has an intimation of a solution of this question. At the Cleveland blast furnaces pig iron has been produced and sent by rail in tanks out to the works at Newburgh, six miles away; there they have been poured into a large tank capable of holding—I don't know how many tons. Perhaps Mr. Richards can tell.

PROF. J. W. RICHARDS: About a hundred and fifty tons.

MR. E. R. TAYLOR: That is done, primarily, to equalize the different products from hour to hour of the blast furnaces. It seems to me that a modification of this could be adapted to the steel question, and immediately from the blow of a steel run to a tank of very much larger capacity than several charges from the Bessemer converter or electric furnace, and there allowed to settle in its own sweet way. In that way a settlement could be obtained beyond anything you have ever considered. Being the first chemist for several years for the Cleveland Rolling Mill Company, which was one of the predecessors of the American Steel and Wire Company, I met this question of slag in the Bessemer steel very early in the day. They made a great deal of wire at that time, though nothing as compared to now, and the inclusion of slag in the wire was brought constantly before us. I sometimes wonder how slow one's thought is, and how I might have suggested a greater time between the blow and the pouring of the metal into the ingots. (Applause).

MR. F. N. SPELLER: Mr. Chairman, freeing steel from oxides and slag is a very serious question, as Prof. Richards has pointed out. There are two main factors which may be considered as having important bearing on shortening the length of time required to clean up the steel while it is in the ladle. In the first place a suitable slag must be present with ample capacity for absorbing the oxidized products. In the second place, ample circulation of the steel in the ladle so that all of the metal may be brought into intimate contact with the slag. I have made a

considerable number of experiments in regard to these influences in purifying the steel and it is quite an important part of our present practice to maintain a thorough circulation of the steel in the ladle for a few minutes prior to teeming into the molds.

One way of illustrating the rapid reaction under these conditions is to put some low melting point cinder which is practically free from the oxides of iron and manganese on the surface of the molten steel in the mold immediately after teeming. This will form a molten slag, and as there is always active circulation in the mold in the case of low carbon steel it will be found in a few minutes that the slag has absorbed a large proportion of its weight of oxides of iron and manganese from the steel.

DR. AMBERG: If I understood Mr. Rodgers right, he said the question was not quite settled whether slag was of such great importance in wire. Did I understand that right?

MR. RODGERS: I think you misunderstood me. I would add a word more, in regard to the question of slag. We think, just as Mr. Speller has already stated, that the slag inclusions are very important and largely dependent on the condition of the slag when the steel is taken from the furnace, as well as the rate of pouring. We know that the general physical condition of the slag has a great deal to do with the amount of inclusion. The question of time comes in, as well as the subsequent circulation which has been referred to in Mr. Speller's remarks as being very important.

DR. AMBERG: I thought Mr. Rodgers' experience was chiefly based on wire production, or generally speaking, on materials where the ingot had been chiefly stretched in its length direction. In that case, of course, the effect of slag in the finished product is not quite as harmful as in forgings or castings which have to stand transverse tests. In these cases the slags are much more serious.

Mr. Sinding-Larsen will find on page 12 of this paper in the Proceedings of the Congress (p. 138 of these Transactions) that I did mention the oxidizing removal of sulphur, to which I dedicated extensive experiments along the line of Aschermann's patent. They are described in "Stahl und Eisen," 1904, No. 7.

A paper presented at the XXII General Meeting of the American Electrochemical Society, in Joint Session with Sections IIIa: Mining and Metallurgy; Xa: Electrochemistry, and XIb: Conservation, of the VIII International Congress of Applied Chemistry, in New York City, September 10, 1912. Dr. Wm. H. Walker in the Chair.

THE DETERMINATION OF OXYGEN IN IRON AND STEEL BY REDUCTION IN AN ELECTRIC VACUUM FURNACE

By Wm. H. Walker and Walter A. Patrick.

At the fifth meeting of this Congress held in Berlin in 1903, F. Lurman presented a paper on the determination of oxygen in iron and steel, in which he pointed out the necessity of a new method which would measure the total oxygen in the sample, and especially that portion which is combined with manganese, aluminium, silicon, and the other oxides not reducible with hydrogen. Since that time no advance has been made in this important field of metallurgical work.

The important role which the oxides of iron and the other metals play in determining the physical and chemical properties of iron and steel was first clearly brought out by Prof. Ledebur in 1882. At this time Ledebur proposed the analytical method for determining oxygen which bears his name and which is based upon the reduction of the oxide at a red heat by hydrogen, and weighing the water thus formed. Owing to the fact that at a high temperature hydrogen reduces only the oxides of iron, leaving unattacked to a large extent the oxides of manganese, aluminum, silicon, titanium, etc., it is obvious that the method is not a satisfactory one, although up to the present the only one available for the purpose.

Other methods have been proposed for determining the oxygen in iron and steel, based upon the solution of the constituents which are not oxides. As examples may be mentioned the method of dissolving the sample in ether solutions of iodine or bromine: or that based upon the volatilization of the iron in a stream of chlorine gas at a high temperature; but none of these methods has proven of any value.

Although the detrimental effect of combined oxygen in iron and steel has been known since the time of Ledebur's first paper,

it is only within the last few years that the full significance of these effects has been appreciated. That iron oxide can exist in iron and steel in more than one form seems certain, and that the oxides of the different metals associated with iron should have characteristic effects is surely to be expected. But in the absence of any satisfactory analytical method for determining the oxide present, the relation between cause and effect has been of necessity very uncertain. It is hoped that the method of deter-

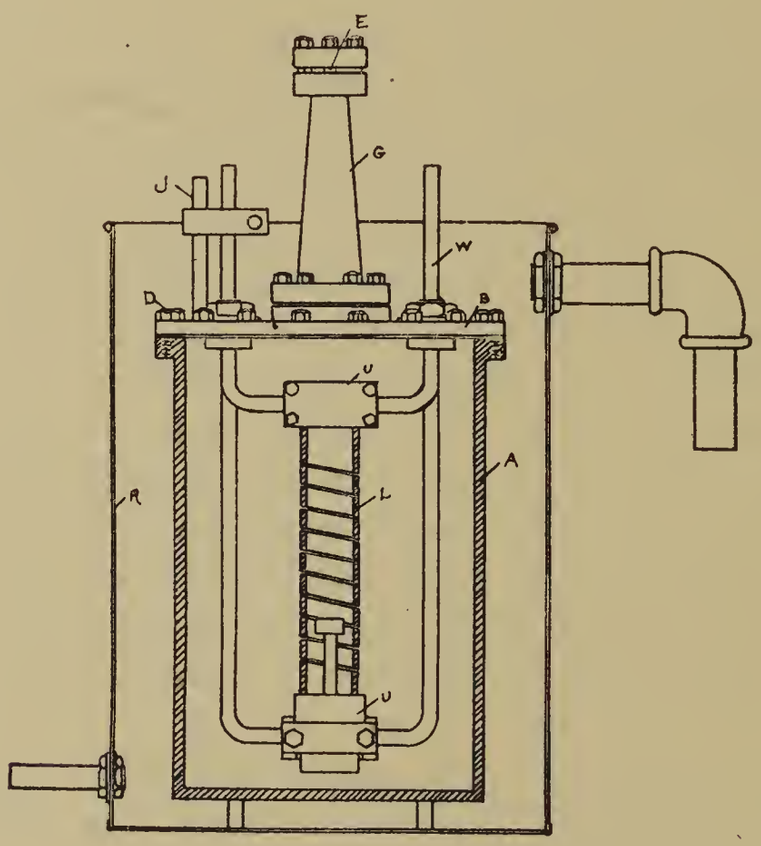


FIG. 1.

mining oxygen now to be described will be an aid in establishing the connection between the oxygen content and the physical and chemical properties of iron and steel.

In the now well-known reaction wherein the oxides of the elements are converted into the corresponding carbides by heating them with an excess of carbon to a high temperature in an electric furnace, the oxygen is given off quantitatively as carbon monoxide. The quantitative formation of carbon monoxide is aided by an excess of carbon at high temperatures, and by a low pressure; also, as has been pointed out by Moissan, the refrac-

tory oxides are more readily reduced in the presence of metallic iron.

The details of the method as at present worked out are as follows:

A vacuum furnace of the Arsem type as supplied by the General Electric Co. is employed, and is shown in Fig. 1. The gun metal chamber *A* of the furnace of 20 cc. capacity rests inside the waterjacket *R*. The cover *B* is fastened to the chamber by means of 18 cap screws *D*, and the joint is made tight by a rigid lead gasket. The tube *J*, through which the air is exhausted is soldered into the cover. The window tube *G* is fastened to the cover by six cap-screws, the joint made tight by another lead washer. The mica window *E* is placed in the top of the window tube. Current is led in through the electrodes *W*, which are brass tubes containing running water. The graphite heater *L* is fastened to the electrodes by means of the clamps *U*. The crucible is supported by the stand as shown in the figure and is thus placed in the hottest part of the furnace.

Twenty to twenty-five grams of the sample of metal in which the oxygen is to be determined is placed in a small graphite crucible and about four or five grams of finely powdered graphite added. The crucible is then placed in the furnace, the cover bolted down, and by means of a small rotary oil pump operated in series with a Geryk pump a vacuum of 0.01 mm. is obtained in the furnace in less than fifteen minutes. After thoroughly exhausting the furnace, the cooling water is turned on and the crucible and contents heated to about 500°–600° with the pump still running. This is necessary in order to remove as completely as possible the oxygen absorbed by the heater and crucible. As carbon does not begin to reduce the oxides below 900°, there is no danger in heating the crucible up to 500°. After fifteen minutes the furnace is allowed to cool, which it does very rapidly. Nitrogen that has been dried over sulphuric acid and phosphorus pentoxide is now allowed to enter the furnace until the latter is about half full. This is then pumped out and the crucible again gently heated. Only by such a treatment is it possible to reduce the oxygen left in the furnace to a reasonably small value. It seems impossible to pump the absorbed oxygen entirely out of

the furnace, but by washing with dry nitrogen it can be almost eliminated.

The stopcock leading to the pump is now turned off, and seventy volts applied to the electrodes, which causes a current of about 200 amperes to flow through the heater. A high temperature is reached very rapidly, the metal melting in three or four minutes. Just as the metal melts violent ebullition very often occurs. This is prevented by opening the circuit for a short time and allowing the charge to cool. The metal soon

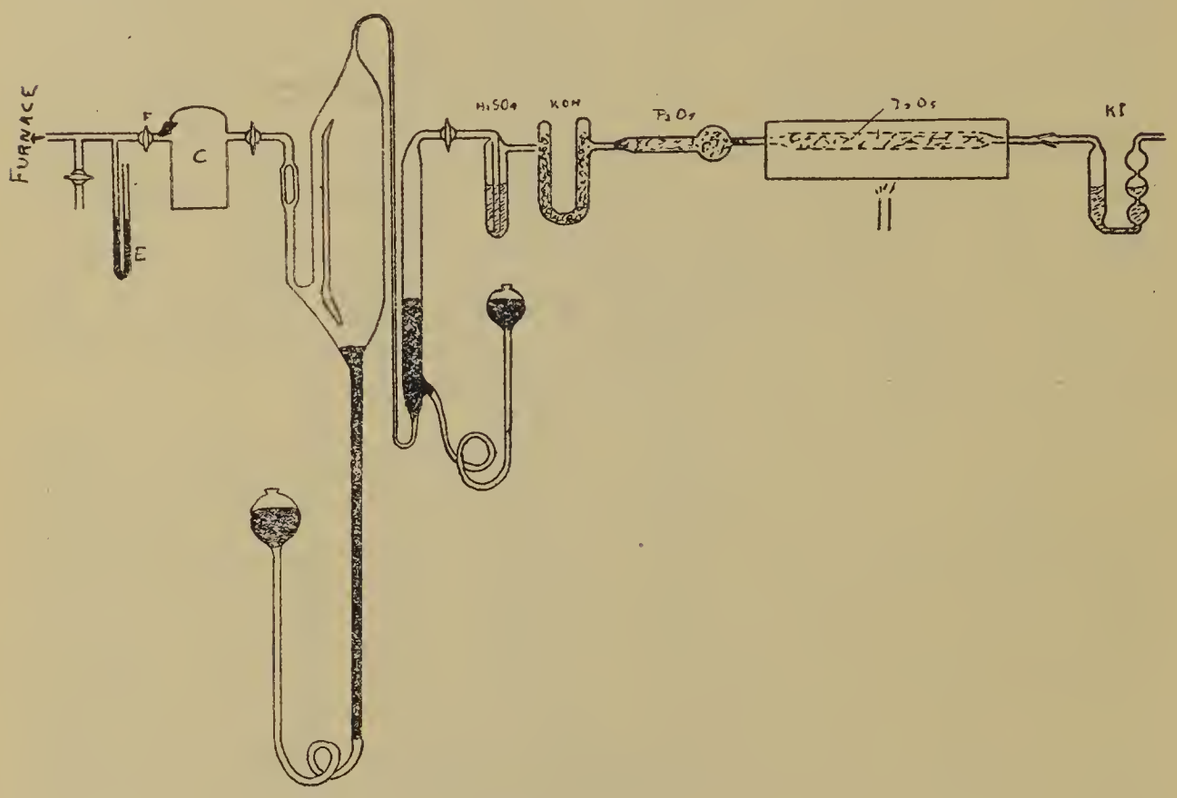


FIG. 2.

becomes quiet and the heating is continued for twenty minutes. The furnace is then allowed to cool thoroughly, after which fresh air, or better nitrogen that has been dried over sulphuric acid and phosphorus pentoxide, is allowed to completely fill the furnace.

The gas now in the furnace is analyzed for carbon monoxide in the following manner:

The vessel *C* in Fig. 2 is exhausted by means of a Toepler pump, and connections made with the furnace as shown in the diagram. The stopcock from the furnace is opened and if the gas in the furnace is under a pressure other than atmospheric, the

difference is shown by the differential gauge *E*. Correcting the barometric pressure by this amount gives the pressure of the gas inside the furnace. Stopcock *F* is now opened, and the vessel and the pump filled with gas. A decrease in pressure corresponding to the volume of gas taken from the furnace is shown by the gauge *E*, and we are thus able to calculate the fraction of gas taken from the furnace. By this method we are practically free from any errors due to temperature variation.

The gas is now slowly forced over iodine pentoxide which is heated to 130°C. and here the carbon monoxide is oxidized to carbon dioxide, liberating an equivalent amount of iodine. The latter is absorbed in a 10 percent solution of potassium iodide and subsequently titrated with N/100 sodium thiosulphate.[1]

A much more simple method of withdrawing an aliquot part of the gas for analysis, if a large quantity of mercury is available, is to use a mercury aspirator instead of the Toepler pump. By replacing the reservoir *C* by a liter bottle which may be filled with mercury, a known fraction of the contents of the furnace may be withdrawn, and forced directly through the iodine pentoxide tube.

The first point to be definitely determined was, how free from oxygen can the furnace and its heating element be made; in other words, using a sample of iron known to be free from oxygen, what amount of oxygen will be shown in a blank experiment? It was found that the oxygen indicated by the iodine liberated from the iodine pentoxide was due to three factors: first, a certain practically constant amount of iodine set free from the iodine pentoxide when air or nitrogen free from carbon monoxide was led over it; second, the actual oxygen absorbed on the walls and on the heater of the furnace; third, the moisture in the furnace.

That iodine pentoxide when heated to 150° in a current of dry air or nitrogen would give up small amounts of iodine has been recognized by previous investigators.[2] We have found that by reducing the temperature to 130° the oxidation of the carbon monoxide is complete, while the decomposition of the pentoxide is reduced to a minimum. By withdrawing from the furnace at each analysis a constant volume of gas and drying the same over

[1] Nicloux and Gautier, Compt. Rend. **126**, 746.
Kinnicut and Sanford, Jour. Am. Chem. Soc., **22**, 14.
[2] L. A. Levy, Jour. Soc. Chem. Indus., **30**, 1437.

phosphorus pentoxide, a uniform blank amounting to 0.006 grams oxygen for the furnace contents was obtained. The weight of oxygen absorbed on the walls of the furnace and in the heater when a vacuum of 0.01 mm. was maintained was found in blank analysis using iron free from oxygen to be 0.02 grams. If the air used to dilute the furnace contents previous to withdrawing the sample of gas for the carbon monoxide determination be not dried over phosphorus pentoxide, the amount of oxygen indicated may rise to 0.035 grams. By first exhausting the air from the furnace, and then filling with nitrogen and re-exhausting, the amount of oxygen shown by a blank analysis was found to be between 0.0120 and 0.0129 grams.

The accuracy of the method, so far as the ability to carry out the operations without introducing errors not corrected for as above, was shown by the fact that a sample of iron or steel containing oxygen may be heated, the oxygen determined, and upon reheating the same charge with additional carbon no further formation of carbon monoxide is obtained.

To determine the accuracy with which the oxygen of a sample of iron or steel will be converted to carbon monoxide, a number of analyses were made using an iron of very low oxygen content, and adding known quantities of the various oxides in the pure form. In addition to iron oxide, only the very refractory oxides of aluminum and silicon were used; other easily reducible oxides such as manganese and copper will introduce no difficulties. The weighed amount of the pure oxide together with a known weight of iron was placed in the graphite crucible and covered with powdered graphite and heated as described. From the oxygen as determined was substracted that due to the blank and the iron and the following results were obtained:

	Weight of Oxide	Oxygen Calculated	Oxygen Found
Ferric oxide	0.5650 gr.	0.1695 gr.	0.1700 gr.
" "	0.6525	0.1960	0.1940
" "	0.8400	0.2520	0.2440
" "	0.1516	0.0455	0.0480
Aluminium oxide	0.4925	0.2310	0.2040
" "	0.1860	0.0875	0.0810
" "	0.3065	0.1440	0.1260
Silica	0.0673	0.0360	0.0342
"	0.0320	0.0181	0.0171

While the results as obtained are not so accurate as is desired, the reduction being somewhat incomplete, and therefore the results uniformly low, the method has served to explain the discrepancies noted between the oxygen content as determined by the Ledebur method in certain samples and their physical and chemical properties. As examples of such analyses may be mentioned the following:

Sample No. 1 is a special heat of an open hearth steel to which iron ore and an excess of manganese were added in the ladle. The finished steel gave every evidence of having a high oxygen content, although, by the Ledebur method, but 0.006 percent oxygen was obtained. When determined by the vacuum furnace reduction method the real oxygen content of the steel proved to be 0.20 percent.

Sample No. 2 is a high grade of open hearth steel in which the Ledebur method detected no oxygen. The vacuum method showed that there was 0.09 percent present.

Samples No. 5 and 6 represent two ingots from the same heat of open hearth steel of high quality. To No. 5 was added some iron oxide as the ingot was poured. The oxygen content of the ingot giving satisfactory results was 0.065 per cent, while that to which the ore was added and which was highly unsatisfactory proved to be 0.31 percent.

Nos. 11a and 11b are duplicate analyses of an ingot iron of early manufacture. The vacuum furnace method indicates about three times as much oxygen as the Ledebur method. 12a and 12b are ingot iron of later make and show an oxygen content of but 0.10 percent. The full analyses are given in the following table.

No. 1. Open hearth steel to which manganese and ore were added.
No. 2. Good quality of open hearth steel.
No. 3. Open hearth steel.
No. 4. Same heat as No. 3, but from ingot to which ore was added.
No. 5. Open hearth steel. Ore added to ingot.
No. 6. Same heat as above. No ore.
No. 7. Open hearth steel.
No. 8. Open hearth steel.
No. 9. Open hearth iron.
No. 10. Open hearth iron.
No. 11a. Ingot iron. Early manufacture.
No. 11b. Ingot iron. Early manufacture.
No. 12a. Ingot iron.
No. 12b. Ingot iron.

No.	C	Mn	S	P	Si	Cu	O Ledebur Method	O Vacuum Furnace
1	0.19	0.92	0.052	0.123	....	....	0.006	0.29
2	...	...	....	....	....	....	0.000	0.09
3	0.17	0.65	0.097	0.064	0.017	....	....	0.11
4	0.12	0.17	0.065	0.088	0.015	....	....	0.33
5	0.09	0.18	0.061	0.087	0.019	.....	....	0.31
6	0.14	0.24	0.070	0.092	0.009	.....	....	0.065
7	0.09	0.33	0.065	0.068	0.006	0.17	0.009	0.021
8	0.08	0.33	0.036	0.070	0.005	0.22	0.010	0.039
9	0.01	0.03	0.050	0.007	0.003	0.20	0.037	0.056
10	0.01	0.04	0.015	0.008	0.004	0.19	0.052	0.064
11a	0.01	trace	0.015	0.002	....	.....	0.069	0.23
11b	0.01	trace	0.015	0.002	....	.....	0.076	0.21
12a	0.02	0.03	0.029	0.004	0.0014	0.043	...	0.10
12b	0.02	0.03	0.029	0.004	0.0014	0.043	...	0.11

It is intended that this paper be considered a preliminary communication, and it is hoped that the method will be both simplified and improved by further work. It is published at this time in the hope that others interested in the effect of oxygen on steel will find in the idea something of value.

DISCUSSION.

MR. SINDING-LARSEN: In methods such as this it is necessary that the gas used be absolutely dry. If it is not dry, or at one time more dry and at another less dry, we have a variable factor which makes for error, and not a constant error. Anhydrous phosphoric acid is not sufficient as a drying means; if you take gas that has passed very slowly over this and then let the gas pass over a surface of clean alkali metal you will see at once that the metal gets a film of alkali. I have found a method by which I can have such an indifferent gas absolutely dry. I make an alloy of potassium and sodium in equivalent molecular weights. This alloy is liquid. If I take such a liquid alloy in an ordinary washing bottle, and let the gas slowly pass through, I have a real dry gas.

DR. W. H. WALKER: I think that is a most useful suggestion. I thank Mr. Sinding-Larsen very much for it.

MR. PRATT: What time is required to make a determination of oxygen?

DR. WALKER: When the apparatus is all set up, it takes about half an hour to get the furnace ready and ten minutes to make the melt, and I should say a half hour to finish it, possibly two hours.

DR. R. AMBERG: When reading through this paper it occurred to me whether the results obtained by the Ledebur method indicated perhaps only part of the oxygen, which is constitutionally different from the rest. Is it possible that the Ledebur method might perhaps indicate the metallic oxygen, oxygen in solid solution in metal, and the total includes all the oxygen contents in gas or other non-metallic form, such as slag enclosures and the like?

DR. WALKER: The carbide method or vacuum method does, I think, take all the oxygen. I do not think there is much doubt about that. I do not know that I have any reason to think that the oxygen as obtained by the Ledebur method does not include those oxides which are reducible by hydrogen. That is rather a theoretical consideration which I do not believe I have the data to answer definitely. Has anyone any opinion on that?

PROF. JOSEPH W. RICHARDS: I believe the Ledebur method will give the oxygen present as CO and dissolved FeO, while it would not give the oxygen present as silica, alumina, manganese oxide or calcium oxide; these latter are decomposed and give up their oxygen in the electric furnace determination. MgO does not form carbide when heated at high temperatures; therefore it would not give up oxygen in the electric furnace determination.

The method of Mr. Sinding-Larsen for drying gas is very excellent, but perhaps expensive, and I think it would be best to first dry the air as thoroughly as possible by a cheaper reagent, and then finish the drying by means of the liquid alloy. There is a reagent which is probably much cheaper than phosphorus pentoxide, and that is thoroughly calcined alumina, which, ac-

cording to a note published lately in the Journal of the American Chemical Society, will, when thoroughly calcined, absorb moisture up to eighteen percent of its weight, and so effectually that after passing through the calcined alumina the gas gives up no further moisture to P_2O_5. Assuming that statement true, that is a much cheaper way of drying the gas than using phosphorus pentoxide.

A paper presented at a Joint Session of Section Xa: Electrochemistry, and Section Ve: Paints and Pigments, of the VIII International Congress of Applied Chemistry, in New York City, September 11, 1912.

MILL SCALE AS A CAUSE OF THE PITTING OF STEEL PIPES

By George C. Whipple and Melville C. Whipple.

Steel seems destined to come more and more into use as a material for the construction of water conduits of certain size. For small pipes, say up to a diameter of about three feet (90 cm.), cast iron has proved most satisfactory and economical. As the size increases above this point, cast iron meets a formidable competitor in steel, for, although this metal costs more than cast iron, it is stronger and the pipe may be thinner. The use of steel is increasing, and it would increase more rapidly if engineers did not fear that corrosion would limit the life and perhaps cause the failure of the pipe line. Cast iron has been tried for many years, and experience has shown that it has a long, useful life that may be depended upon. Some wrought iron pipes also have lasted well. Steel pipes have been used for a shorter period. In general they, too, have retained their useful life, although in some cases, where they have been exposed to exceptionally severe conditions, they have given trouble. A number of steel pipe lines have developed leaks, due to the corrosion of the metal in spots, that is, to pitting. In this respect steel appears to differ from wrought iron, over the surface of which the rusting is more uniform. In fact, it is this tendency to pit that engineers chiefly fear. Steel pipes almost never fail completely by breakage, as cast iron pipes sometimes do; they merely leak through the small holes or pits produced by corrosion, so that failure would come about as a gradual process. Nevertheless, leaks are always undesirable, and many leaks, or a large leak, may be serious.

The general subject of the corrosion of steel has been carefully considered during the last few years, and the relative advantages of different grades of steel and iron have been much discussed by engineers, chemists and manufacturers. Some have claimed that wrought iron and steel were equally durable; some have claimed

decided advantages for that form of mild steel known as American ingot iron, on account of its low manganese content and the general resemblance of its chemical analysis to that of wrought iron; while some have claimed that the presence of small amounts of copper in steel tended to make it resist corrosion. In these discussions the importance of one factor has been very largely overlooked, namely, that of the mill scale, and, as far as the use of steel for pipe lines is concerned, attention has been diverted from an important element of the problem. Although it is generally accepted by text-book writers that pitting is closely connected with the presence of mill scale, and that steel from which mill scale has been removed does not pit, the salesmen of the steel companies, and even the chemists themselves, have much to say about the absence of manganese and the presence of copper, and very little to say about the nature of the mill scale or whether this scale is or is not affected by the purity of the metal. It is to call attention to this neglected phase of the subject that the present paper has been prepared.

Occasion of the Investigation.

In November, 1911, Mr. E. A. Fisher, City Engineer of Rochester, N. Y., requested one of us to undertake an investigation to ascertain the relative merits of steel, American ingot iron and wrought iron for the construction of a 66-inch sewer outlet 9,000 feet long into Lake Ontario. This pipe is to carry the effluent from sedimentation tanks through which the sewage of the city is to be passed before being discharged into the lake at a point 7,000 feet from the shore.

Through the courtesy of Mr. Emil Kuichling, Consulting Engineer to the City of Rochester for this project, samples of steel, wrought iron and ingot iron were secured from the Allegheny Steel Company. Later, through the courtesy of Mr. C. F. W. Rys, Metallurgical Engineer of the Carnegie Steel Company, and Mr. V. Browne and T. G. Siexas, of the Allegheny Steel Company, samples of steel containing known amounts of copper were secured. Other samples were obtained at various places.

Nature of the Experiments.

At the beginning, a few simple immersion tests were made. Samples of the steel and iron were placed in jars of distilled

water, Brooklyn tap water, salt solutions, solutions of chloride of lime, dilute acids, strong acids, etc., and observations and analyses made to determine the relative amounts of corrosion of the different samples. The results were of some interest, as noted below, but, practically speaking, it was found that they could not be relied upon to tell which metal would act best when submitted to the conditions expected at Rochester. The immersion tests in tap water and dilute solutions progressed too slowly, while the use of strong solutions failed to reproduce in the laboratory the conditions that would be met in actual practice. Difficulties also arose in controlling the oxidation of the iron in the solutions after it had been dissolved in the ferrous condition. This was influenced by the volume of the solution used, the ratio of the volume to the surface of water exposed to the air, and several other factors, as Friend has well shown in his recent book on "The Corrosion of Iron and Steel."

Finding that the ordinary accelerated tests, using strong acids, were unreliable so far as the problem at hand was concerned, a different kind of accelerated test was tried, namely, one in which corrosion was stimulated by a current of electricity, that is, an electrolysis test. This was not employed for the purpose of observing those phenomena of corrosion that ordinarily occur when stray currents from high voltage electric lines find their way to a pipe line or other steel structure. On the other hand, the currents employed were much stronger than would be set up in a pipe line by galvanic action, and so did not reproduce the actual conditions of service, but they enabled corrosion to take place in natural water and weak, dissociated solutions under conditions similar to those that would be found in the pipe line carrying sewage. It was thought that this test would also show the manner of corrosion, as distinguished from the total amount of corrosion, better than the acid tests, and, inasmuch as the real question at issue was one of pitting, and not one of general rusting, the electrolysis test seemed to be a more reliable one for the case at hand.

The results of the application of this test to various samples of steel showed clearly that mill scale has a marked influence on the uniformity of corrosion and the formation of pits. This suggested possible differences in the electrical condition of the

mill scale on the different samples of steel submitted to us, and an investigation of this feature was also undertaken.

Description of Steel Samples.

The following notes show the nature of the samples used in the experiments:

A. Steel received from Emil Kuichling, furnished by the Allegheny Steel Company.

11 pieces 6″ x 2″ x ⅜″ (15 x 5 x 1 cm.).
Surface covered with black scale.

Analysis (by Dr. J. C. Olsen):

	Percent
Carbon	0.16
Manganese	0.31
Silicon	0.03
Copper	0.002

B. Ingot iron received from Emil Kuichling, furnished by the Allegheny Steel Company.

11 pieces 6″ x 2″ x ⅜″ (15 x 5 x 1 cm.).
Surface covered with scale, which is almost black, but slightly brown.

Analysis (by Dr. J. C. Olsen):

	Percent
Carbon	0.02
Manganese	0.01
Silicon	0.02
Copper	trace

C. Wrought iron received from Emil Kuichling, furnished by the Allegheny Steel Company.

11 pieces 6″ x 2″ x 2/8″ (15 x 5 x 0.6 cm.).
Surface covered with black scale, on which there was a slight film of yellowish brown iron rust, which could be easily rubbed off.

Analysis (by Dr. J. C. Olsen):

	Percent
Carbon	0.07
Manganese	0.19
Silicon	0.04
Copper	0.001

D. Charcoal iron boiler tubes received from Allegheny Steel Company.

3 pieces 6″ (15 cm.) long cut in half lengthwise from 2″ (5 cm.) tubes. These pieces were covered with a rather thick black scale, somewhat heavier at some points than at others. The surface presented the fibrous, stringy appearance common to wrought iron.

E. Steel boiler tubes received from Allegheny Steel Company.

3 pieces 6″ (15 cm.) long cut in half lengthwise from 2″ (5 cm.) tubes. The scale was black and fairly uniform in distribution and thickness.

F. American ingot iron boiler tubes received from the Allegheny Steel Company.

3 pieces 6″ (15 cm.) long cut in half lengthwise from 2″ (5 cm.) tubes. The scale on these pieces was black, with a small amount of red oxide on the surface, not as much, however, as the American ingot iron usually has.

G. American ingot iron sheets received from the Allegheny Steel Company.

12 pieces 2″ x 8″ x ⅛″ (5 x 20 x 0.3 cm.).

These pieces presented a dark surface covered with scratches, which probably resulted from the removal of most of the scale by a wire brush. The general character of the surface was smooth.

H. American ingot iron plates received from the Allegheny Steel Company.

12 pieces 2″ x 8″. Gauge 10.2. (5 x 20 cm.)

The surface of these samples was covered with a scale containing a large proportion of red oxide, giving them the appearance of rusted pieces. The scale was not very thick, but uniform in distribution. The red oxide easily rubbed off on the hands.

I. Hot rolled steel plate received from shop in Pierce Hall, Harvard University.

6 pieces 2″ x 8″ x $\frac{3}{16}$″ (5 x 20 x 0.5 cm.).

This steel had a black, tightly adhering scale of varying thickness, often occurring in layers or "scales."

J. Carbon steel plate from Carnegie Steel Company.
12 pieces 2½″ x 8″ x ¼″ (6 x 20 x 0.6 cm.).
Heat number, 13,121.
Analysis:

	Percent
Copper	0.0
Carbon	0.10
Phosphorus	0.011
Sulphur	0.024
Manganese	0.38

These samples, as well as those listed under *K* and *L*, were stamped with the heat number. The scale around the edges was irregular in distribution, owing to abrasion during shearing. It was black, rather glossy in appearance, and fairly smooth and regular in the surface presented, except at the edges, as mentioned above.

K. Copper steel plate received from Carnegie Steel Company.
12 pieces 2½″ x 8″ x ¼″ (6 x 20 x 0.6 cm.).
Heat number, 23,583.
Analysis:

	Percent
Copper	0.23
Carbon	0.07
Phosphorus	0.011
Sulphur	0.028
Manganese	0.38

L. Copper steel plate from Carnegie Steel Company.
12 pieces 2½″ x 8″ x ¼″ (6 x 20 x 0.6 cm.).
Heat number, 23,778.
Analysis:

	Percent
Copper	0.53
Carbon	0.11
Phosphorus	0.10
Sulphur	0.025
Manganese	0.43

Immersion Tests.

In the first experiment strips of steel *A*, ingot iron *B* and wrought iron *C*, as received, were put in separate beakers containing distilled water and allowed to stand at room temperature

(70° F. = 21° C.). The distilled water contained 3.5 parts per million of CO_2 and was saturated with oxygen. After 24 hours the water in the beaker that contained the ingot iron had less color than the other two, and analysis showed that it contained less iron.

	Steel *A*	Ingot Iron *B*	Wrought Iron *C*
Area of metal wetted, sq. cm...	23	22	22
Quantity of water, cc.....	370	375	395
Iron in water, mg. per litre.....	45	14	36

Samples of steel *A*, ingot iron *B* and wrought iron *C* were next placed in beakers containing distilled water and tap water, and allowed to stand for various periods of time, during which the appearance of the plates was noted and analyses of the water made to determine the amount of iron present in the ferrous and ferric condition. Variations in the conditions were secured by using hot and cold water and by comparing strips of steel from which the mill scale had been removed with similar strips with the mill scale left on except at the edges. Detailed records of these experiments were kept, but the results do not warrant publication, as they were so erratic that it was evident that all of the necessary conditions of the experiment had not been properly controlled. Suffice it to say that all three metals rusted badly in all of the experiments, and that such differences as were noted between the different metals were due more to experimental errors than to the character of the metals themselves. Generally speaking, the rusting was slightly greater in the case of the metals from which the mill scale had been removed than in these cases of the metals on which the scale had been left, but in this comparison the differences were somewhat less with the wrought iron than with the steel or ingot iron. At the start the mill scale on the steels appeared to exert a slight protective action, but after a few days this disappeared. On the whole, the ingot iron showed somewhat smaller losses of iron than the other metals, but this was not true in all of the experiments, and the differences were never large.

After immersing samples of the three metals in weak N/50

sulphuric acid, N/50 acetic acid and a 10 percent solution of bleaching powder and obtaining heavy corrosion in all cases, the plates were examined under the microscope to see if any differences in the scale could be detected. The appearance of the scale of the American ingot iron was not greatly altered by the immersion, although a large amount of it had disappeared, exposing the metal beneath. The steel plates showed less loss of scale, but under the microscope the scale surface exhibited minute cracks and fissures, and in places small holes, through which the iron beneath had passed into solution, as evidenced by the deposit of red oxide close to these openings. These openings in the scale were much more numerous after immersion than before. The appearance of the wrought iron scale was not materially changed by immersion, but such loss of scale as occurred was uniform over the surface of the test piece.

Electrolysis Test.

When two plates of iron are immersed in water and connected in circuit with a battery a current of electricity will pass through the water from one plate (the anode) to the other (the cathode), and iron will be dissolved from the anode; in other words, the anode will corrode. If the plate forming the anode is uniform in composition, the corrosion will be uniform over its surface, and the loss in weight will be proportional to the current density. If the anode is not homogeneous in character, the density of the current will not be uniform over the plate, and the corrosion will be greater at some spots than at others. Thus no corrosion at all will occur over areas where some such insulating material as coal tar has been spread, but will occur in greatest degree where the raw metal is exposed.

The mill scale that is formed upon the surface in the manufacture of steel differs in chemical composition from the metal beneath it, being composed largely of iron oxides, together with some slag, and it is to be expected that its electrical resistance would be different. Moreover, the mill scale commonly occurs not as a sheet of uniform composition and thickness, but as a series of flakes or scales (hence its name), sometimes overlapping and varying greatly in thickness. This is often evident to the eye, but may be better observed by the use of a lens. Hence,

when a sheet of steel covered with mill scale is used as the anode, it might be naturally expected that the current density would vary and that the corrosion of the metal would occur not uniformly, but in spots. Conversely, if the corrosion produced by passing a current of electricity between electrodes is irregular, it may be inferred that the scale is not homogeneous in thickness or quality; and, further, that if different plates act differently when submitted to such a test, the inequality of the character of the scale will be measured by the irregularity of corrosion. These ideas were well illustrated by a series of experiments performed as follows:

Two plates each of steel *A*, ingot iron *B* and wrought iron *C* were arranged in pairs in separate jars of water, parallel to each other and three inches (7.5 cm.) apart, and connected in parallel with an Edison-Lelande battery, the potential of which was found to be 0.88 volt. Each jar contained 2,100 c.c. of Brooklyn tap water (hardness 37.5, alkalinity 15.5, chlorine 12.0, carbonic acid 5.0 parts per million). The plates were thickly coated with paraffin except that exposed surfaces 3 inches (7.5 cm.) long and one inch (2.5 cm.) wide were left facing each other in each pair of plates. At first no change occurred, but after one hour the ingot iron appeared to be rusting in spots and the wrought iron in streaks, the steel showing no sign of corrosion. After 1.5 hours, and again after 21 hours, samples of the water were withdrawn from each jar and analyzed for iron, with the following results:

Increase in Iron in Parts per million :	After 1.5 hours	After 21 hours
Water in jar containing the steel.....	0.3	2.9
" " " " " ingot iron	1.2	3.3
" " " " " wrought iron ...	1.5	6.1

After 24 hours the physical differences between the three plates were conspicuous; the wrought iron was rusting in streaks that nearly covered the entire surface, while the steel and ingot irons were rusting in spots, one particular spot on the steel being especially noticeable.

In order to hasten the action, a stronger direct current from a lighting circuit was then applied (55 volts and 0.2 ampere) and tap water allowed to flow freely through the jars, being directed

against the exposed areas in order to prevent the accumulation of gas at the anode plate. After three days the plates were examined. All were covered with rust, but when this was removed it was found that the wrought iron had corroded uniformly without pitting, but that both the steel and the ingot iron were badly pitted, the steel being the worst.

A second series of tests was then made using other plates of the same lots of steel, ingot iron and wrought iron, but with the mill scale removed in each case by grinding on an emery wheel. Submitted to a current of the same strength and for the same length of time, these plates corroded uniformly and without any sign of pitting. The wrought iron plate appeared to be slightly grooved, the steel plate showed a slight tendency towards a honeycombed structure, while the ingot iron plate was smoothly etched and had a bright, silvery surface.

In order to corroborate these results the experiments were repeated using other pieces of metal, both with and without the scale, using a lighting current of 112 to 120 volts, and 0.12 to 0.18 ampere for four days; also with the current reduced to 2 volts and 2 milliamperes for 22 days. In this case the samples used were *A, C, E, G, H, I, J, K, L.* The results were the same as those first obtained, namely, the test pieces from which the scale had been removed did not pit, but rusted evenly. The wrought iron with the scale on did not pit, but corroded in grooves, the metal showing in general a uniform fibrous surface. The steel samples with the scale on and the ingot iron samples pitted, the pitting in the steel samples being invariably the deeper.

In certain of the plates holes were then drilled through the scale at regular intervals and the experiment repeated, thinking that corrosion might take place exclusively at these points. This was not found to be the case. Pits did occur at these points, but they also occurred at other points, indicating invisible fractures or openings in the scale. The number and depth of the pits differed in different samples of steel and ingot iron.

The loss of weight by rusting in these experiments did not differ greatly with the different materials, but, comparing the slight differences, the loss was greatest in the case of the wrought

iron and least in the steel, as illustrated by the following figures, which show the loss in weight of different plates exposed for 22 days to a direct current of 2 volts and 2.0 to 2.8 milliamperes.

Sample	Volts	Current Milli-amperes	Loss in weight grams per square centimeter
A Steel	2	2.8	0.013
B Am. ingot iron	2	2.0	0.015
C Wrought iron	2	2.0	0.017

The electrolysis test therefore serves to indicate the *manner* in which plates corrode rather than the *amount* of the corrosion. Inasmuch as it is the pitting with which the water works engineer is chiefly concerned, this form of accelerated test appears to have some advantage over immersion tests in which strong corrosive acids are used. In these strong acids the action is essentially a chemical one, but in the dilute solutions used with the electrolytic tests, the strict chemical action is subordinated to the electrolytic form of corrosion. This test, therefore, more nearly approaches the conditions of natural corrosion in water.

It has frequently been observed that with the ordinary acid tests the purer forms of metal show the smaller losses. This is strictly a chemical action, in which the mill scale, as well as the iron, is dissolved away. With the electrolysis test, however, the purity of the metal itself exerts less influence, and the scale remains for a longer period of time, to become an important factor as it does in actual service. Mention has been previously made of the fact that mill scale may exhibit marked differences of potential toward iron, due largely to its varying composition and thickness, which influence the resistance offered to the passage of an electrical current.

Galvanic Survey of the Mill Scale.

According to the electrolytic theory of corrosion the solution of the iron is brought about by the action of currents that are set up between different particles of the metal that have different electrical potentials, as, for example, between the pure metallic iron and various impurities such as carbon, manganese, slag, etc. This has been illustrated by Walker, Cushman and others by the

use of the ferroxyl indicator. Purity and homogeneity, therefore, tend to diminish corrosion. It is believed that pits in steel occur at points where for some reason or other there are particles that have greater differences of potential from that of the metallic iron or the mill scale than are found elsewhere on the sheet. Possibly this may result from segregation of the impurities during the cooling of the ingot; possibly it is due to the effect of rolling, cooling and other treatment the mill scale undergoes. It is known, at any rate, that differences of potential exist between iron and its oxides, and it seems reasonable to believe that this is a very important cause of pitting, perhaps the most important factor of all.

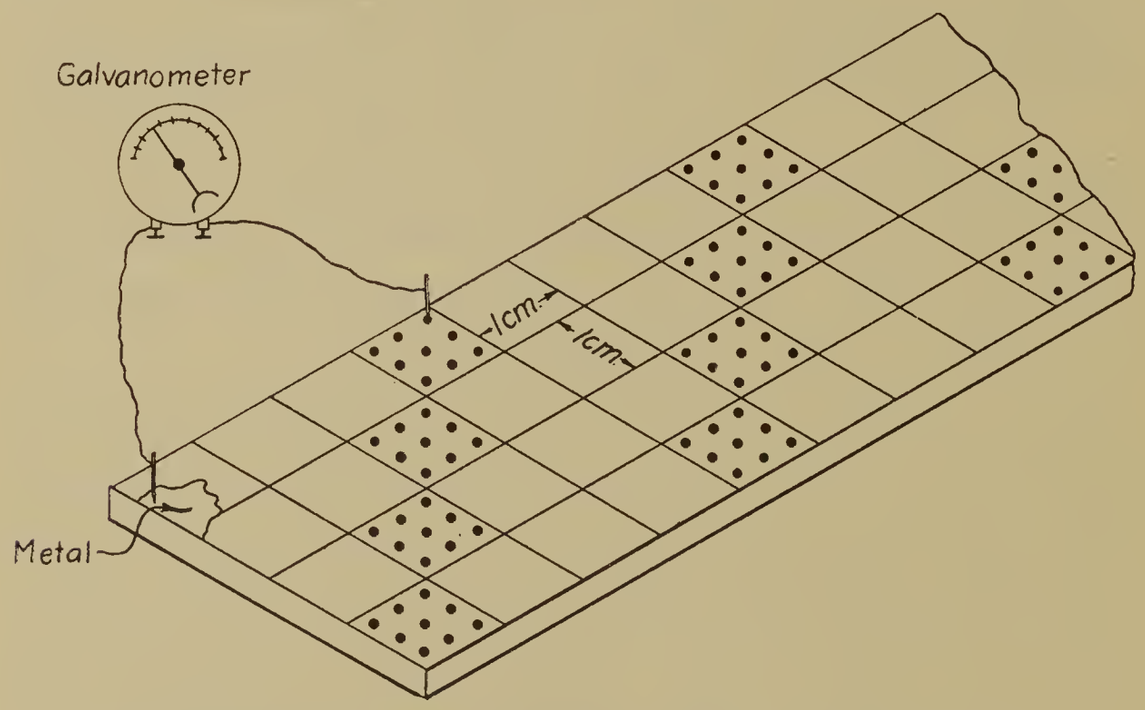


Fig. 1.
Method of Making Galvanic Survey of Scale on a Sample of Steel.

It seemed to us, therefore, that a study of the potential differences between the mill scale at different points and the raw metal beneath might throw light on the relative liability to pitting of the various metals submitted to us for study. On account of the difficulty of making the necessary measurements with the samples immersed in water, the simple method was adopted of connecting the raw metal of a sample with its mill scale by means of wires and placing a very sensitive galvanometer in the circuit, the two contact poles being the rounded ends of No. 18 (1.6 mm. diam.) copper wire. The galvanometer used was sensitive to less

than one ten-millionth of an ampere. It was found that when both poles were put in contact with raw metal no current could be detected, but that when one pole touched the raw metal and the other pole touched the scale on a piece of steel plate a noticeable current was set up, which in some cases amounted to nearly one-millionth of an ampere. Usually the current in the galvanometer circuit was from the scale to the metal, and in the sample from the metal to the scale, that is, in the direction which would tend to make the iron dissolve. Occasionally, however, the current was in the other direction. On the steel plates the currents sometimes differed greatly at points only one millimeter apart;

		0.8 0 0.8 0.8 1.5 5.9 1.5 3.0 1.6			1.7 3.2 2.7 0.4 1.0 3.7 2.1 0 3.5
	2.6 2.6 1.7 2.0 4.5 1.5 0 0.3 0.7			1.9 3.2 3.3 0.7 1.2 2.5 1.5 0.8 1.5	
2.6 0.3 0.4 1.4 3.9 1.9 4.6 0.8 2.6			0.5 2.7 1.5 1.6 0 3.3 0 0 0		

Fig. 2.
Results of a Galvanic Survey of a Sample of Steel Plate. Figures Show Current in Amperes $\times 10^{-7}$

more often, however, there were areas where the current was relatively high and others where it was relatively low. Very slight currents were found in the case of wrought iron and cast iron, indicating a great homogeneity of the scale or less difference of potential between it and the metal.

Studying the mill scale of a steel plate with the microscope and comparing the observations with the current readings it was evident that to a considerable extent the current varied with the thickness of the scale, but occasionally decided differences of current were found between points on the scale that looked exactly alike. It was noticed that when one pole was touched to raw metal and the other to red rust (Fe_2O_3) little or no current

was produced; and the greatest currents were set up between the raw metal and the black scale (magnetic oxide), the brown scale on ingot iron giving results intermediate between the other two.

In order to compare the different samples submitted to us, areas of one square centimeter were marked out in squares, and what may be called a galvanic survey made, nine spots being tested in each square as shown in Figs. 1 and 2. As a rule about 200 galvanometer observations were made for each plate

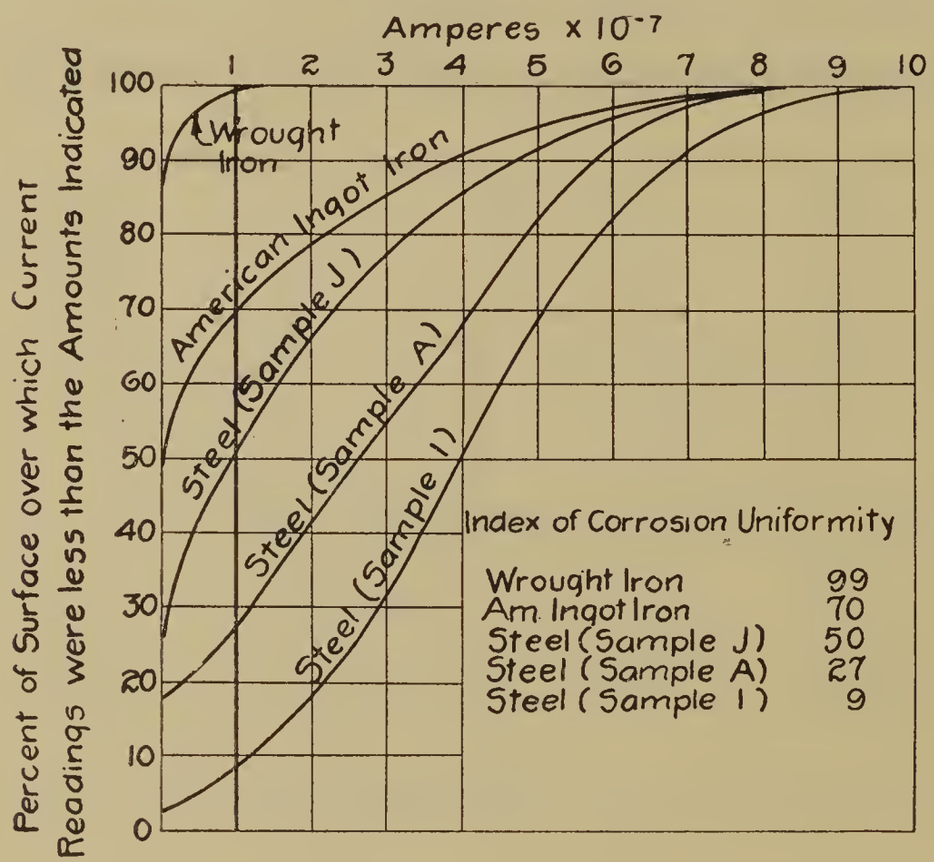

Amperes x 10⁻⁷
1 2 3 4 5 6 7 8 9 10
100 90 80 70 60 50 40 30 20 10 0
Percent of Surface over which Current Readings were less than the Amounts Indicated
Wrought Iron
American Ingot Iron
Steel (Sample J)
Steel (Sample A)
Steel (Sample 1)
Index of Corrosion Uniformity
Wrought Iron 99
Am. Ingot Iron 70
Steel (Sample J) 50
Steel (Sample A) 27
Steel (Sample 1) 9

Fig. 3.

Diagram Showing the Method of Finding the Index of Corrosion Uniformity.

tested. The results were then tabulated and the percentage of observations found for currents of different strength. It was assumed that this presented the percentages of the areas of the scale where currents of these strengths were likely to be set up. With the plate immersed in water the actual strength of the currents would be different from those observed, and probably greater. The results, therefore, must be considered as having a relative value only.

In order to better compare the different plates the percentages

of area where the current found was less than certain strengths were then added together serially, and these figures were tabulated and plotted with the strength of current as abscissae and the percentages of areas as ordinates. Typical curves based on the average of several surveys in each case are shown in Fig. 3 for wrought iron, ingot iron, ordinary mild steel and a steel which was found to pit badly. It will be seen that the differences between these curves are very striking, the wrought iron showing a much lower and more uniform current than the ingot iron or steel. In making this summation the points where the current was found to flow from the scale to the raw metal were included with the points where there was no current, as it was assumed that at these points no solution of the iron would occur.

Index of Uniformity of Corrosion.

If the uniformity of corrosion over the surface of a scale-covered plate varies with the uniformity of the current set up between the scale and the metal at different points, a figure representing this uniformity of current may be considered as a sort of index of corrosion uniformity. If the current is the same at all points, or if no current is shown by the galvanometer between the raw metal and all points on the surface, the index may be taken as 100. This is the case of plates from which the scale has been removed. If practically no current is found over 75 percent of the area, the index of uniformity may be taken as 75, and so on. The difference between 100 and this figure is therefore an index of the liability to irregular corrosion or pitting.

As the galvanometer readings were not accurate below one ten-millionth of an ampere, and as very minute currents are of less effect than stronger currents. the percentage where no current was found did not appear as fair a criterion for estimating this index as the percentage where the current was less than one ten-millionth of an ampere ($A \times 10^{-7}$). In other words, a current of this magnitude was considered as practically negligible. For the purposes of this comparison, therefore, the index of corrosion uniformity was taken as the percentage of the surface area of the plates over which the galvanic current was found to be less than one ten-millionth of an ampere, while the index of pitting was taken to be 100 less this percentage. These values

are purely arbitrary, but serve to provide a basis for a comparison of the tendency of different samples to pit. Illustrations of these values are given in Fig. 3, where the curves show the index of corrosion uniformity and its index of pitting to be as follows:

	Index of Uniformity	Index of Pitting
Wrought iron	99	1
American ingot iron	70	30
Steel	50	50
Pierce Hall steel	9	91

The current values from which these curves were plotted represent the average of several samples.

In order to determine the accuracy of this method of making readings and computing the index of corrosion uniformity, duplicate tests were made upon certain samples several weeks after the first ones, with the following results:

	Index of Uniformity		Index of Pitting	
	1st Test	2d Test	1st Test	2d Test
Wrought iron *C*	99	100	1	0
Steel *K*	66	64	34	36
Steel *L*	58	60	42	40
Steel *I*	9	2	91	98

Fig. 4 shows the curves obtained for two samples of steel that differed considerably. It will be seen that they correspond quite closely at the point which has been chosen to determine the index of corrosion uniformity.

Thinking that the amount of moisture and occluded gases within the pores of the scale, or between the scale and the metal, might influence the galvanic currents flowing, samples were dried for two hours at 100° C., and then subjected to readings with the galvanometer. These tests did indeed show less current flowing between the scale and metal after moisture had been driven off, and the index of corrosion uniformity was consequently raised somewhat by drying the sample. In the case of wrought iron the index was increased from 99 to 100; in the case of steel from

58 to 72 (see table). Results obtained after soaking samples in water and drying did not differ materially from those made with samples under ordinary atmospheric conditions. The reduction of moisture content obtained in the drying experiments represented a greater percentage variation than any which would occur in ordinary atmosphere. Accordingly it was considered satisfactory to compute the index of uniformity for a given sample from tests made under ordinary atmospheric conditions.

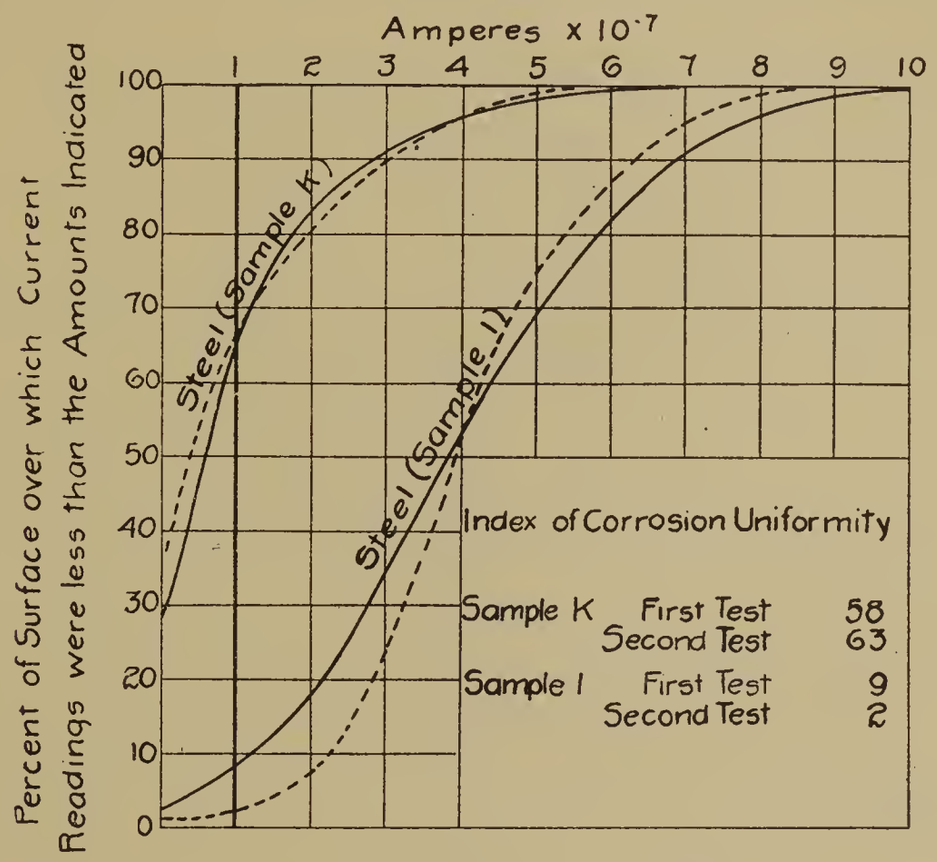

Amperes x 10⁻⁷
1 2 3 4 5 6 7 8 9 10
100 90 80 70 60 50 40 30 20 10 0
Percent of Surface over which Current Readings were less than the Amounts Indicated
Steel (Sample K)
Steel (Sample I)
Index of Corrosion Uniformity
Sample K First Test 58
Second Test 63
Sample I First Test 9
Second Test 2

Fig. 4.

Diagram Showing Results of Duplicate Galvanic Surveys of two Samples of Steel.

Relation Between Pitting of Plates and the Index of Corrosion Uniformity.

In order to see whether there was any relation between the index of corrosion uniformity and the actual pitting as induced by the electrolysis test a piece of metal that had been carefully surveyed and found to have a low index of uniformity, *i. e.*, a high index of pitting, was placed in a beaker of tap water and connected as the anode with a similar plate, while a 116-volt direct current was sent through the battery. On observing the plate

closely with a lens it was seen that rusting began first at the points where the current had been found below the average for the plate, and the irregularity of the formation of iron oxide was marked. A plate that had a high index rusted more uniformly.

Percent of Surface Area Over Which the Observed Galvanic Current Was Less Than the Figures Indicated.

Amperes × 10-7.

Sample	0	1	2	3	4	5	6	7	8
Wrought Iron.									
C1	81	99	100						
C2	70	98	100						
American Ingot Iron.									
B	54	72	80	88	94	98	99	100	100
H1	36	55	68	78	86	91	96	98	100
H2	55	82	88	92	95	97	98	98	100
Steel.									
A	17	27	42	55	68	82	92	97	100
I	3	9	18	34	53	67	82	91	97
I Duplicate	2	2	9	24	56	74	87	96	99
J	26	50	68	84	91	94	97	100	100
K	36	67	80	90	96	99	100	100	100
K Duplicate	29	63	84	95	97	98	99	100	100
L	18	58	71	81	87	91	95	98	100
L Duplicate	11	62	82	92	98	99	100	100	100
L dried at 100° C.	15	72	93	99	100	100	100	100	100

The appearance of plates representing the three metals tested, namely, wrought iron, ingot iron and steel, has already been described under the electrolysis test. The tendency to uniform corrosion varied with the index of uniformity, the plates which gave an index of 98 or 99 being practically free of pits, while the plates which had an index of 50 to 75 showed marked pitting.

Other evidence of the general nature of the action over the surface of plates with high index of uniformity was provided by the general disappearance of scale. This was in marked contrast to the deeply pitted plates, where the bright metallic surface was exposed only for a short distance around the centers of pitting. The following figures show the relation between the index of corrosion uniformity and the number and depth of the pits that developed under the electrolysis tests under comparable conditions:

Sample	Index of Corrosion uniformity	Index of Pitting	Number of Pits per Sq. Inch	Depth of Pits in mm.		
				Max.	Min.	Avg.
Wrought iron	98	2	3.6[1]	0.6	1.4	1.0
American ingot iron	70	30	6.8	1.6	3.2	2.1
Steel	50	50	10.0	1.3	3.5	2.2

[1] These were grooves rather than pits.

When corrosion occurs in plates immersed in water through the differences of potential between scale and metal it would appear necessary to have the water come in contact with both the scale and the metal in order to furnish the necessary electrolyte and supply oxygen for the oxidation of the iron. This introduces another factor, namely, the porosity of the scale. To some extent this porosity is probably taken into account by the galvanometer test. Microscopical examination of the scales showed in many instances the presence of minute cracks through which water might enter and come in contact with the metal. In general these cracks were more numerous in those samples that showed a low index of corrosion uniformity. In some of the steels the appearance of the scale resembled a clayey soil after being sun-dried, that is, it was covered with hair cracks. In others the scale had the appearance of microscopic beds of lava.

On the whole it may be said that the index of corrosion uniformity as determined by the galvanic survey of the scale appears to give a fair measure of the probable liability of the surface of the metal to corrode in an irregular manner, that is, to pit.

Experiments with Copper Steels.

That manganese, sulphur and some other impurities likely to be found in steel stimulate its corrosion is the conclusion of a number of observers. This is particularly true if these impurities are irregularly distributed throughout the mass of the metal. It is unnecessary to review the theoretical reasons advanced for this belief further than to say that they are based on the electrolytic theory of corrosion, and deal with the changes in conductivity and resistance produced within the metal by these impurities. It has been claimed that some other metallic elements when present in small quantities have an opposite effect upon corrosion, that is, that they retard action. Chief among these is copper. Campbell[2] says that copper occurs as an impurity in many steels, particularly those made by the Bessemer process, and may be present to the extent of 0.3 to 0.5 percent.

Opinion seems to be divided in regard to the effect of copper in retarding corrosion. There is evidence to show that it materially decreases the solubility of steel in sulphuric acid, but the question arises as to its effect upon the electrical properties of the steel. Sang[3] states that the depolarizing effect of the electronegative metals, such as copper and lead, might be expected to hasten the rusting of iron or steel. If copper protects, and if steel ordinarily contains as much copper as Campbell has stated, then it is rather surprising that the copper steels have not given better service.

The samples tested (*J, K* and *L*) contained 0, 0.23 percent and 0.53 percent of copper, respectively. The use of copper steel having been suggested for the Rochester sewer outlet pipe, some experiments were undertaken to determine its advantages, if any, for this service. These included immersion tests, electrolysis tests and galvanic surveys.

Immersion Tests with Copper Steels.

Strips of the metal, 2½″ x 8″ (6 x 20 cm.) were buffed and cleaned of dirt and grease, weighed and placed in glass trays, supported upon four ⅛″ (0.3 cm.) pieces of the same metal.

[2] Metallurgy of Iron and Steel, p. 358.
[3] Sang, Corrosion of Steel, p. 37.

450 cc. of 25 percent sulphuric acid, enough to completely immerse the strips, was then poured into the tray. Twice during a period of 24 hours this acid was renewed and the solution was stirred occasionally. At the end of 24 hours, the plates were removed, washed, dried and weighed. In the case of sample *J*, which contained no copper, the action had been violent, as evidenced by the evolution of hydrogen and the bright etched surface of the plate. Sample *L*, which contained the most copper, showed the least action, as far as surface appearance indicated. The following losses in weight were obtained. The loss in weight is seen to be much greater in the steel that contained no copper than in the other two.

Immersion Test with 25 Percent Sulphuric Acid.

Sample	Percent of Copper	Loss in Weight in Grams	Area Exposed in Sq. Cm.	Loss of Weight in Grams per Sq. Cm.
J	0	27.0	307	0.0880
K	0.23	5.4	270	0.0200
L	0.53	5.1	258	0.0198

The effect of a dilute sulphuric acid solution was also tried. For this purpose an N/50 solution of acid, (*i. e.*, about 0.1 percent) was used, the cleaned plates being placed in two-quart glass jars and covered with the acid. After 26 days the following losses of weight were found:

Immersion Test With N/50 Sulphuric Acid.

Sample	Percent of Copper	Weight in Grams	Area Exposed in Sq. Cm.	Loss in Grams per Sq. Cm.
J	0	3.00	234	0.0128
K	0.23	2.90	247	0.0117
L	0.53	3.15	231	0.0136

These results were in marked contrast to those in which the stronger acid was used, as they showed only slight differences between the losses from metals containing different amounts of copper.

Immersion tests were also made using sodium chloride solutions of two strengths, namely, 0.3 percent and 3 percent, the latter having a salinity about equal to that of sea water. The losses in weight after 26 days were as follows:

Immersion Tests With Salt Solutions.

Sample	Percent of Copper	Loss of Weight in Grams per Sq. Cm.	
		3 Percent Solution	0.3 Solution
J	0	0.0015	0.0013
K	0.23	0.0015	0.0019
L	0.53	0.0019	0.0021

The general results of the immersion tests go to show that where the action is emphatically a chemical one, as in the case of the strong acid test, the presence of copper tends to reduce the action; but where, as in the tests with weak dissociated acids and salt, the electrolytic form of corrosion predominates, copper does not reduce corrosion, but on the other hand, tends slightly to stimulate it.

Electrolysis Tests of Copper Steels.

Electrolysis tests of the copper steels were made, according to the method previously described. A lighting circuit was the source of current, and the plates were arranged in separate jars in the form of batteries connected in parallel with the anode and cathode separated by a distance of three inches. A low current of 2 volts and about 2 milliamperes was first used, a resistance coil being employed for the reduction of the current. This test extended over a period of 22 days, during which running tap water passed constantly through the jars containing the plates. The following losses in weight were recorded:

Electrolysis Experiment With Low Current For 22 Days.

Sample	Percent Copper	Voltage	Current in Milliamperes		Loss of Weight in Grams per Sq. Cm.
			At Start	At Finish	
J No. 13,121	0	2	2.5	2.5	0.0072
K No. 23,583	0.23	2	3.2	2.9	0.0082
L No. 23,778	0.53	2	3.2	3.0	0.0080

Sample *J*, which had no copper, was found, upon inspection after the test, to have developed pits of considerable depth at various places on the surface. Except around these pits the scale remained intact. Samples *K* and *L* showed a somewhat larger area of general corrosion and most of the pits were not as deep as in the case of *J*. Less of the original scale remained on these plates.

Another test was made with these steels using a 112-volt current. This experiment extended over a period of 51 hours. Readings at the start showing a current strength of 0.23 to 0.25 ampere, and at the close 0.17 to 0.18 ampere. An examination of these plates showed that all of them had been subjected to irregular action with the formation of pits. Samples *J* and *K* presented much the same appearance, patches of black scale adhering to the plate in patches where the action had not exposed the bright metallic surface. The latter was rough and irregular in contour, the result of uneven loss of metal. The exposed metal of Sample *L*, which contained the most copper, had a dull lustre owing to a larger number of small pinhole pits. Some of these extended quite as far into the metal as did the larger pits on *J* and *K*, and gave to the plate a honey-combed appearance.

Galvanic Survey of Copper Steels.

The index of corrosion uniformity for samples *J*, *K* and *L* varied between 51 and 67; that is, they did not cover a very wide range. Sample *J*, with 0 percent copper, had the lowest index, namely 51, and consequently the highest index of pitting; and, so far as observed, the electrolysis tests showed that this steel possessed a slightly greater tendency to localized action than

the others, particularly under the influence of a low current for a long period of time. The differences, however, were not marked.

Conclusion as to Copper Steels.

From the tests made it was concluded that the presence of small amounts of copper in steel, while they may retard corrosion by strong acids, do not serve to protect the steel against corrosion in weak acid solutions or in ordinary water. The presence of copper does not materially alter the electrical conditions of the scale, and does not, therefore, protect the metal against pitting.

Conclusion as to Ingot Iron.

The samples of American ingot iron plates tested were found to have an index of corrosion uniformity somewhat higher than that of ordinary steel plates, with or without copper, but lower than that of wrought iron. So far as failure by pitting is to be feared, therefore, the ingot iron may be regarded as somewhat better than steel, but probably not enough better to justify any great difference in cost. Exposed to severe acid corrosion, ingot iron is probably more serviceable than steel, but under ordinary conditions of corrosion in soil or water, it has only a slight advantage over steel.

Conclusion as to Wrought Iron and Steel.

Wrought iron has a very much higher index of corrosion uniformity than steel or ingot iron and is much less likely to pit. This seems to be in accord with experience. Under conditions of severe chemical corrosion, sufficient to remove the mill scale and silicates, or under conditions of atmospheric corrosion, when the electrolytic form of corrosion does not predominate, there is probably little difference between the two metals.

Effect of Removing the Mill Scale.

A partial removal of the mill scale tends to increase corrosion, as it gives opportunity for electrolytic action between the scale and the raw metal. Scale becomes chipped off in handling and in fabrication.

The complete removal of the mill scale from steel plates increases their index of corrosion uniformity from about 50 to nearly 100 and this reduces materially the danger of pitting. The electrolysis tests made with steel plates, from which the mill scale was removed, did not show pitting in a single instance. Scale removal appears, therefore, to be a secure method of protection against pitting. To some extent it has been practiced, the mill scale being removed by pickling in acid, by sand blasting, etc. These processes unfortunately are expensive, but may be justified under some conditions. Steel of ordinary quality with the mill scale removed will probably withstand pitting better than the more expensive ingot iron and copper steels, and just as well as wrought iron itself.

It is possible that some method may be found to modify the mill scale during manufacture so as to make it more uniform or improve its electrical condition, or make it more easily removable. It certainly seems as if the next step in advance in steel manufacture lies in securing a better control of the character of the mill scale. An extended study and series of experiments on the formation, composition and electrical properties of scales produced at different temperatures might determine the conditions that must be controlled to produce a satisfactory scale. If a satisfactory scale cannot be obtained the only apparent remedy for pitting is scale removal.

SUMMARY.

It is the opinion of the authors that the experiments and observations outlined in the foregoing pages warrant the following tentative conclusions relative to short time tests for corrosion, and to the part played in corrosion by mill scale.

(1) Accelerated corrosion tests of iron and steel plates made by immersion in strong acid solutions are of little value as indicating the probable corrosion of the metals in water under conditions of actual service.

(2) Accelerated tests made in running water by the use of a current of electricity give results that indicate the *manner* in which the plates will probably corrode in service; that is, whether by pitting or by general corrosion.

(3) When steel pipe lines fail, they do so by the formation of numerous pits that ultimately form holes and cause leaks. An important factor in the formation of pits, commonly recognized but by no means fully appreciated, is the mill scale.

(4) Steel plates that pit badly under the electrolysis test when the scale is left on do not pit after the scale has been removed.

(5) A galvanic survey of the mill scale, made by determining the current that will pass through a sensitive galvanometer placed in the circuit of wires that connect the mill scale with the metal beneath, gives results that differ materially for wrought iron and steel, and from which an index of the uniformity of corrosion may be calculated that bears a general relation to the liability of the metals to form pits.

(6) The electrolysis tests and the galvanic survey show that wrought iron has a less tendency to pit than steel, and that American ingot iron is intermediate between the two, but resembles steel more nearly than it does wrought iron.

(7) Steels containing copper differ but slightly among themselves and from steel that contains no copper, in their tendency to form pits.

(8) To protect steel or ingot iron against failure by pitting, the best remedy is the removal of the mill scale. Efforts should be made to reduce the expense of doing this, or to modify the character of the scale during its manufacture. This appears to be the direction in which future improvements in the manufacture of steel plates for pipe-lines should lie.

DISCUSSION.

Dr. A. S. Cushman: No one can deny the truth of Mr. Whipple's statement that the presence of mill scale on the surface is one of the important factors that have to be considered in relation to the corrosion of iron or steel. In fact, this point has been frequently referred to in a number of publications by myself and other investigators. At one time I even went so far as to recommend to naval engineers that boiler tubes that have to endure very intensive service should be polished inside with the

same care given to gun barrels, for I had concluded that not only the mill scale but anything leading to a roughening of the surface tended to stimulate corrosion effects. I am sure that all those of us who have been studying this intricate subject for a number of years agree that the mechanism of the corrosion reactions presents a complex problem into which a number of important factors enter. One difficulty that is encountered in corrosion investigations is that results which are obtained under one given set of conditions of test and observation are not always confirmed by tests on the same material made under different conditions. Again, the work carried out by one investigator may not be in agreement with the result obtained by another, although the work may have been equally earnest and carried out with equal care. This has often been a source of discouragement to workers in this field, and there are certainly too many modifying factors in the problem to enable anyone to draw sweeping conclusions from any one set of investigations made in any one place, no matter how ingeniously they may have been carried on or however earnestly the investigator may have been seeking the truth. Some years ago I carried on a set of experiments in which the conditions were quite similar to those described by Mr. Whipple in his tests, but the results which I obtained did not appear to me to confirm observations I had made under more practical and service-like conditions of exposure.

I would call attention to the fact that experiments made with test pieces totally immersed in a corrosive medium and with a given group of samples may vary widely in their results from the results obtained in the same group of samples freely exposed to the atmosphere. The concentration of acids, salts and dissolved oxygen in the liquid or electrolyte, the condition of the surface with respect to stresses and strains, the general homogeneity of the material are all variables, and unfortunately variables not only between different types or kinds of metals but also between materials made in different mills by the same general processes. Even with respect to materials made in the same mill and in the same furnace but in separate heats or representing different parts of one and the same ingot, variable resistance to corrosion under a given set of conditions is also presented to some extent. Taking all this into consideration, it seems to me

almost unnecessary to have to emphasize the danger of arriving at conclusions from any one given set of laboratory experiments which would seem to point to the superiority of one type of iron or steel for any kind of special service. It seems to me that in drawing conclusions of this kind we must take into account long time tests under service conditions, and the general reputation that different types of metals have gained not only as the result of exposure tests but also as the result of practical application to various conditions of service.

I particularly wish to protest against the conclusion which seems to be drawn from this particular group of tests presented by Mr. Whipple, that wrought iron occupies one end of a scale of excellence with respect to corrosion resistance under total immersion conditions such as exist on the interior of a service pipe line, while steel as such occupies the other end and the commercially pure iron which has been referred to as American Ingot Iron occupies an intermediate position. Such a conclusion is not in accord with the results of a great number of investigations and tests that have been carried on by me or under my supervision for a number of years. There are, of course, irons and irons and steels and steels. Some wrought irons are unquestionably better than other wrought irons, and the same is true of the other types of ferrous materials under consideration. I see no reason to recede from the position I have always taken with respect to resistance to corrosion of the ferrous metals, for I still maintain that homogeneity in the metal, other conditions being the same, is a desirable quality. Almost everyone is agreed that segregation and unequal distribution of impurities is something to be avoided in the manufacture of either iron or steel. One way to arrive at homogeneity is to eliminate the impurities to such a point that there shall not be any left to segregate or to be unevenly distributed in the metal. It has frequently been shown in numerous researches that manganese and sulphur, if both present in a steel, tend to segregate as manganese sulphide. This is by no means always the case, but if such segregation has taken place, there can be no doubt about the fact that such segregation would lead to differences of potential and produce the well known pitting effect. I hold that any manufacturer, whether he makes steel or iron, who is earnestly endeavoring by all means

to reduce the lack of homogeneity in his material and to get away from segregation effects, is certain to bring about an improvement in his material.

Whether one should advise the purchase of ordinary steel, coppered steel or a pure open-hearth iron for a given purpose, taking into consideration the differential in price between these products, does not seem to me to be a proper subject of debate before a meeting such as this. There may still be room for honest differences of opinion in regard to these matters. It is perhaps well known that I am a strong believer in purity where resistance to corrosion is the main object sought, although I am free to confess that some of the more expensive iron alloys may prove in the future to be worthy of manufacture on a large scale where tendency to corrode becomes a heavy fixed charge upon engineering work. In spite, however, of the fact that I believe that purity is a desirable quality, I am quite willing to pay my respects to the steel manufacturers who have by earnest effort improved their products by paying special attention to preventing unequal distribution of impurities and have thereby produced a minimum of segregation.

Mr. R. H. Gaines: Whereas it might be a very simple matter to remove mill scale from laboratory specimens, I would like to ask Mr. Whipple if the authors of the paper studied or if they recommend an electrical method for removing mill scale on a large practical scale where large plates are to be dealt with.

Mr. G. C. Whipple: We have not done that. We hope to continue our investigation of steel corrosion, and that is one of the features that we will take up in the future. At the present time my general impression is that the best way to get rid of the scale is by some form of pickling, followed by lime dipping, but that is a question for the future to decide, and really one for the steel and the iron people to take up for themselves.

Mr. Bradley Dewey: I think that before we drop this paper it ought to be emphasized that the tests which have been brought forward are those for differences in the character of the scale on the materials under test rather than for differences in the materials themselves, for the reason, as noted in the paper, that some of the iron under consideration had a reddish brown scale

rather than the black scale on the steels, and the red oxide shows very little difference in potential between it and the underlying metal.

Those who have had experience with the rolling of plates probably all know that the color of the scale is largely dependent upon the amount of water which happens to be running over the rolls at the time of rolling, and it is therefore very conceivable that the red scale on the samples of "Ingot Iron" was due solely to a slight excess of water on the rolls. This condition might therefore have been brought about in a purely accidental manner and is not at all characteristic of either ingot iron or steel. For this reason these tests have only shown the characters of the mill scales and not the characteristics of the underlying materials. This, of course, is emphasized by the fact that when mill scales were removed none of the materials were found to pit.

Mr. F. N. Speller: Mr. Whipple has, I believe, rendered a distinct service in pointing out again the important influence of mill scale on corrosion. It is something that a number have felt was a determining influence, and is referred to many times in papers and reports of researches. This was brought out as the result of experiments made by us in 1905 ("Steel and Wrot Iron Pipe," Iron Age, March 2, 1905) but engineers as a class have been very slow to appreciate the significance of such surface conditions. Personally I have been a little diffident in emphasizing it for fear that it should be taken as an indication that we were trying to shirk our duty in respect to the quality of the metal; we are all striving to get the utmost uniformity; but nevertheless it seems undoubtedly to be a fact that the predominating influence in corrosion and pitting of iron and steel is the surface factor, *viz.*, mill scale or accidental patches of rust and other foreign matter on the surface. Prof. Heyn said at the Congress for Testing Materials, in discussing this very point, that as a result of his investigations he believed that the effect of the purity of the metal itself had been greatly over-estimated so far as corrosion is concerned. Much light has been thrown on the possible influence of various factors on corrosion in the discussions which have occurred at these International Congresses this year. There has been a more general disposition to accept

as a fact the proposition that surface influences have more to do with the question of pitting than any other one factor, and that does not mean that uniformity in the metal itself is not also an important point.

Passing along to Mr. Whipple's tests, he has considered more particularly individual plates, rather than metal of different kinds rolled on small mills for welded plate. Considering the small number of samples of the material under test, and their small area, it seems to me that the conclusions the author has come to have been rather sweeping. The nature of the mill scale depends very much on the temperature at which the steel or iron is rolled, the amount of water used, the type of mill, and how the metal is cooled afterwards, and a number of other points; for instance, the use of salt, which is common practice in plate mills; so that unless the two classes of material to be compared were rolled on the same mill and under the same conditions of heat, rolling and cooling, I do not see how one can make a comparison. These tests, it seems to me, simply indicate that the samples that Mr. Whipple happened to get show this particular condition, but the area and the number of pieces are very small, and another set of samples rolled under different conditions, although the same in composition, would probably show very different results.

Referring more particularly to the conclusion Mr. Whipple reaches, that wrought iron shows a distinct uniformity in respect to pittings compared to steel, let me again call attention to the results of a number of comparisons which were compiled from tests made in service and presented before the International Congress for Testing Materials last week. (Paper by F. N. Speller, "Comparative Service Obtained with Wrought Iron and Soft Steel Pipe as Water Lines in the United States"). These were not taken from my own investigations altogether, but from various researches made during the last three or four years. The principle employed was to search through hot water lines where corrosion has made itself manifest, for cases where wrought iron and steel had by accident been coupled together and used in the same line. In the past ten years both these materials have been very generally used together in the trade and you do not have to go very far to find such cases in actual

service. The reason for this mixture is easy to understand when it is considered that two stocks of pipe, iron and steel, have usually been carried and in filling orders there was no way to distinguish one from the other when the mill tags where removed.

Therefore in such cases we have the two materials rolled and welded by the same process under identical conditions and subjected to water of the same temperature, quality, and air contents, so that the comparison is an ideal one. I found 150 odd cases of such comparisons on record; that is to say, about 150 cases where both iron and steel had been together in the same line under these conditions, where the extent of the corrosion was measured by the depth of the pitting. On averaging these up the depth of the pitting in the case of the wrought iron was found to be slightly greater than in the case of the steel, although not enough so to be of any importance. But it is significant to note that under such conditions of manufacture and use the iron pitted, to say the least, just as much as the steel. I do not say that the area of pitting was the same, because that is not material. The vital point is the depth of the pitting, the life of the pipe depending on when the first hole penetrated the metal.

It is altogether too early to draw any conclusion as to copper steel for pipe. Extensive experiments which we have under way do not seem to be bearing out Mr. Whipple's conclusions, and I feel that it would have been better if he had qualified these conclusions somewhat, considering the limited material and data on which they are based.

PROF. WM. CAMPBELL: I would like to ask one question in regard to the testing of these steel pipes; on tests where you have what you call mixed lines, or mixed samples, would not a line so made up of partly wrought iron and partly steel screwed together give you electrical contact between those and set up a difference in potential there; whereas if the line were all steel or all wrought iron you would not get that? I should think that might have some influence on the pitting of these samples.

MR. SPELLER: That point, I might say, was fully investigated. There is a small galvanic difference one way or the other, between wrought iron and steel, when in contact, but it is not at all uniform in quantity or sign, and the influence does not extend more

than a quarter of an inch or so away from the point of contact: in making all measurements on the depth of pitting, care was taken to keep well away from the contact, and as the length of pipe was about twenty feet, there was plenty of material to work on without considering that portion in direct contact with the coupling.

MR. JOHNSON: I would like to ask the last speaker how he knew that some of these pipes were pure wrought iron pipes and not a mixture of steel and wrought iron, the probability being that when wrought iron gets into a line accidentally it is not then wrought iron, because evidently no pains have been taken to select pure wrought iron for this purpose.

MR. SPELLER: Analyses were usually made to determine the material by etching the sample and determining the manganese and slag contents, and as a rule the pipes were fairly pure wrought iron. At all events the conclusions drawn represent the general run of pipes sold as wrought iron ten years ago. That is the average length of time the samples had been in service.

MR. JOHNSON: In that case I should say that this conclusion does not apply in any way to pure wrought iron.

MR. SPELLER: I beg to differ there, because the samples of wrought iron which showed the highest impurities were just as badly pitted as those which had a composition more like soft steel—no relation could be found between composition and corrosion.

DR. W. H. WALKER: I note that Mr. Whipple's samples are sometimes made up of a number of pieces of steel from the same source. I would ask whether these pieces are taken from different lots of the product, or are all the pieces bearing the same name from one sheet?

MR. WHIPPLE: That I don't know, Prof. Walker. We simply took these samples as they were sent to us. We fully realize that the number of samples that we experimented with was very small, but we did experiment with more than I described and the results were about the same as those that have been presented.

I want to say also that there are often times when engineers have to draw conclusions from a small number of experiments.

For instance, we had to decide what should be used in this pipe line. So we made such experiments as we could and drew our conclusions from the experiments made. Our only object in bringing the paper before you was that you might become interested in this new method of showing up the different character of mill scales, and of estimating the effect of the scale in causing pitting.

MR. R. H. GAINES: Some comparison has been made here between the durability of wrought iron and steel pipe. I would like again to call attention to the experience with a wrought iron conduit and a steel conduit in the water service of the city of Rochester, N. Y. The use of steel for large conduits is comparatively recent, and the conduit at Rochester is probably one of the oldest in the country.

The wrought iron conduit referred to was laid in 1872-3-4 to bring a supply of water to one of the city reservoirs of Rochester. After about twenty-five years' service six or seven small rust leaks had appeared in this conduit, but no trouble to speak of has occurred since.

In 1892-3-4 a steel conduit was laid for an additional supply from the same source, parallel to the older conduit, and only a small distance away. After six or seven years rust leaks began to give trouble, and by 1907, more than 160 rust holes had appeared in the steel conduit, necessitating extensive and costly repairs. I made a study of the corrosion of this conduit in 1907, a report of which will be found in Volume XIII, Transactions of the American Electrochemical Society. Since my observations were made five years ago, I am informed that four hundred and fifty (450) additional rust leaks have occurred in the steel conduit.

In the meantime, the old wrought iron conduit has continued to give satisfactory service, and any damage from rusting is said to have been negligible.

A paper presented at a Joint Session of Section Xa: Electrochemistry, and Section Ve: Paints and Pigments, of the VIII International Congress of Applied Chemistry, in New York City, September 11, 1912.

AN ELECTROLYTIC METHOD FOR THE PREVENTION OF CORROSION OF IRON AND STEEL.

By J. K. Clement and L. V. Walker.

INTRODUCTION.

According to the electrolytic theory of corrosion, when iron is oxidized in the wet way it first goes into solution as ferrous ions. The ferrous ions are then oxidized by the oxygen present in the water to ferric ions, and are precipitated as ferric hydroxide. Simultaneously with the formation of ferrous ions, hydrogen is liberated on the surface of the iron. The passage of the iron from the atomic to the ionic state, and of the hydrogen from the ionic to the atomic state, is accompanied by a transfer of electricity. The ferrous ions derive from the metal surface a charge of positive electricity, the hydrogen ions give up a charge of positive electricity, and a current flows through the metal from the point where hydrogen is liberated to the point where iron is dissolved.

If iron and a metal having a greater "solution tension" than iron, for example, zinc, be immersed in acid solution and connected externally through a wire, zinc will go into solution, hydrogen ions will be liberated at the iron, and current will flow through the wire from iron to zinc. The potential difference between zinc and iron is opposed to the potential difference between iron and electrolyte and neutralizes the force required to pull the positively charged iron ions away from the negatively charged surface of the iron electrode. Consequently iron does not go into solution.

In place of zinc, other conducting materials, *c. g.*, carbon, may be used as the anode, and the E. M. F. required may be furnished from an external source. In this way electric energy derived from either a battery or a generator may be used to protect metals from corrosion under water.

A vast amount of work, both theoretical and experimental, has been directed to the study of the causes of corrosion and the development of methods for its prevention, and the literature on the subject is extensive.[1]

Very little attention, however, seems to have been given to the development of an electrolytic method for the prevention of corrosion. An electrolytic method has been used to some extent for the protection of boilers.[2] This method consists in submerging a bar of zinc in the boiler water and connecting the zinc electrically with the boiler plates. After the experiments described in this paper were begun it was found that an electrolytic process for the protection of metals had been patented by an Australian inventor.[3] The writers have been unable to find any data published by this inventor.

In a paper presented before the Sydney, Australia, Section of the Society of Chemical Industry, G. Harker[4] describes experiments on the prevention of the corrosion of iron by electrolysis. He determined the current density necessary to prevent the corrosion of steel plates submerged in N/25 H_2SO_4, tap-water, sea-water and "dilute acid." The results of Harker's experiments, which furnish the only data on the subject which the writers have been able to find, will be discussed in connection with the results of our own experiments.

EXPERIMENTS BY F. M. STANTON.

Experiments to devise an electrical method for the prevention of the corrosion of steel immersed in acid water were undertaken at the Pittsburgh Experiment Station of the Bureau of Mines in May, 1911, by Mr. F. M. Stanton.

Stanton's experiments included laboratory experiments and tests on plates immersed in the Monongahela River. In the laboratory experiments, steel plates 6 mm. x 19 mm. x 51 mm. were suspended in N/5 H_2SO_4, in separate vessels. In one vessel a carbon rod was suspended near the steel plate, and connected

[1] See Cushman and Gardner, "Corrosion and Preservation of Iron and Steel," McGraw-Hill Book Co., New York.
"List of References to Books and Magazine Articles on Metal Corrosion and Protection," Bulletin, Carnegie Library of Pittsburgh, July, 1909.

[2] J. H. Paul, "Corrosion in Steam Boilers," Trans. Soc. Engineers, **31**, 147.

[3] See Western Electrician, **58**, 326 (1911).

[4] G. Harker and J. McNamara, "Electrolysis as a Means of Preventing the Corrosion of Iron and Steel," Journ. Soc. Chem. Ind., **29**, 1286 (1911).

to the positive pole of a storage battery, the negative pole of which was connected with the steel plate. The steel plate in the second vessel was not protected. After 24 hours' exposure it was found that the unprotected plate had lost in weight 1.8100 grams, and the protected plate only 0.0012 gram.

In the tests with plates submerged in the Monongahela River a much smaller current density was used than in the laboratory experiment, and the protection against corrosion was much less complete. The plates used in these tests had the following dimensions: 6 x 8 x ⅛ in. (15 x 20 x 0.3 cm.). The protecting current was furnished by a 2-volt accumulator. The loss in weight of the two plates at the end of fifteen days' immersion was, for the protected plate 0.7 gram, and for the unprotected plate 10.9 grams.

EXPERIMENTS TO DETERMINE CURRENT DENSITY REQUIRED TO PREVENT CORROSION.

Mr. Stanton left the service of the Bureau in July, 1911, and the work was interrupted until December, 1911, when experiments were resumed by the present authors and Mr. A. E. Hall.

The object of the experiments to be described was to determine the current density required to prevent corrosion of steel plates in acid water under various conditions.

Experiments with Apparatus Type I.

The first method of determining the protective effect of small currents was to suspend an iron plate of the dimensions shown in Fig. 1 in an 800 c.c. flask parallel to a ¼-in. (0.6 cm.) carbon rod and ½ in. (1.2 cm.) from it. Using storage batteries as a source of E. M. F., a current was passed from the carbon rod through dilute sulphuric acid to the iron plate. The current regulation was accomplished by using variable resistances, and the current measured by the drop in potential over a known resistance, by means of a Siemens and Halske millivolt meter; electrical connections were completed before any acid was introduced into the flask, and the current regulated immediately thereafter. In order to save time, six such flasks were used in each experiment.

The results of the first series of experiments are shown graphically in Figs. 2 and 3. The experiments represented by

the curves in Fig. 3 were made under uniform conditions, except that the duration of the test was varied. These experiments indicated that a definite current density must be maintained in order to reduce the corrosion loss to a minimum. On account of the poor agreement between the results of individual experiments a second type of apparatus was designed.

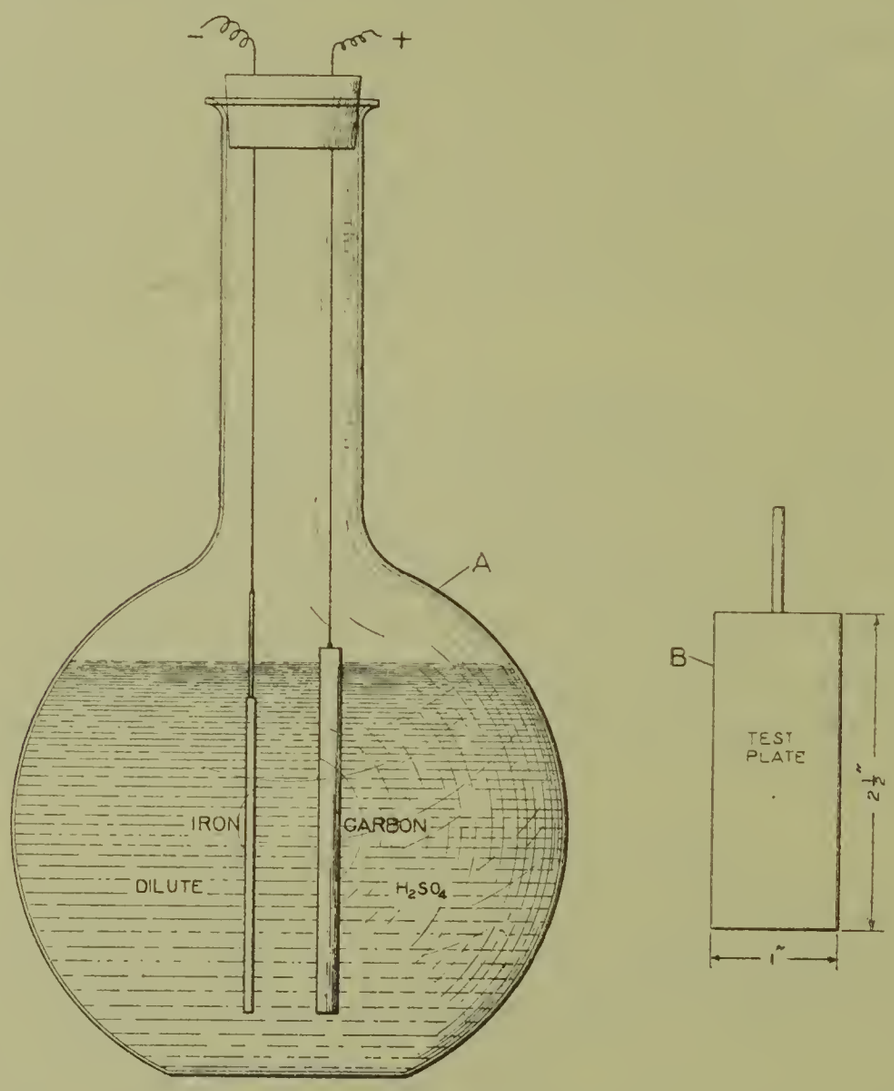


FIG. 1.

Experiments with Apparatus Type II.

In order to eliminate as far as possible any error due to differences in acid concentrations about the iron plates, all the test plates were immersed in a common vessel. Another improvement was the employment of an acid reservoir and a constant level device by means of which fresh acid could be fed into the containing vessel at any desired speed and the excess electro-

lyte syphoned off through the level bottle into the overflow. The vessel was a porcelain-lined cylindrical dish of about 2,250 c.c. capacity, and the plates were supported by a thin wooden cover at points on a circle 4 in. (10 cm.) in diameter, and at whose center the carbon rod anode was suspended. The plates were set equidistant from each other and, of course, from the anode.

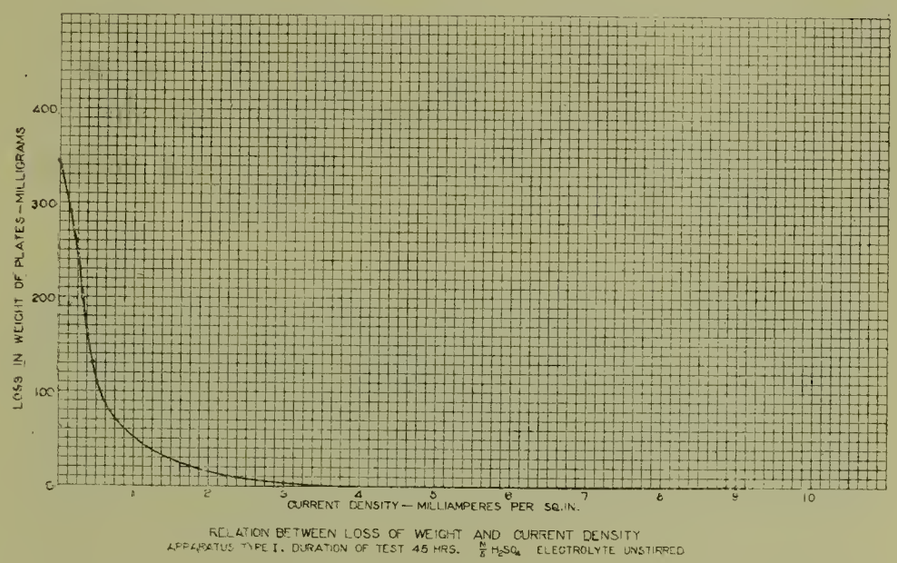


FIG. 2.

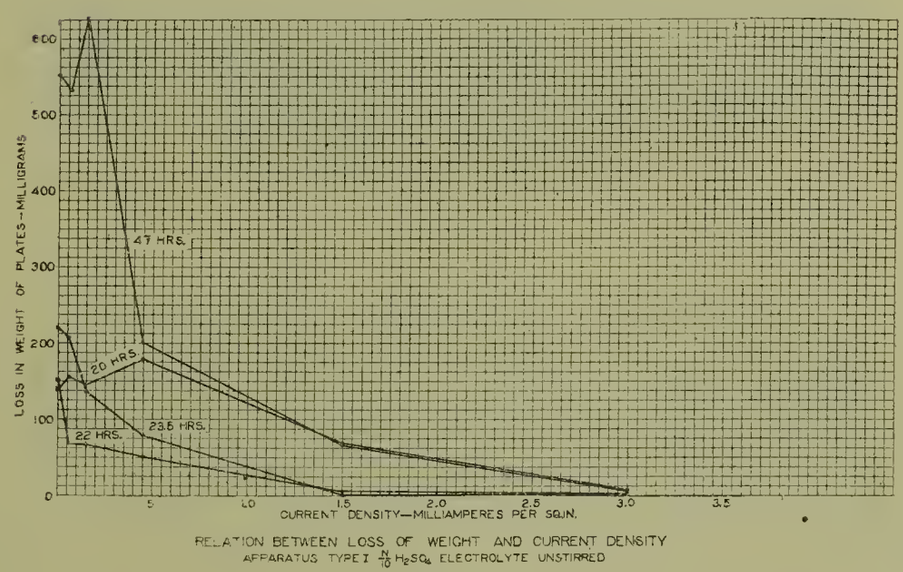


FIG. 3.

Six experiments were conducted according to this scheme, and the acidity of the electrolyte was determined at the end of each run. There was always a considerable falling off in acid strength, which could be eliminated to a large degree by increasing the rate of acid feed. For example, at the end of a 27-hour

run, starting with N/10 H_2SO_4, the acidity was 85/1000 normal. As all the plates, however, were subjected to the same variation in the corrosive element, the loss in weight of the plates should be comparable.

The curves in Fig. 4 represent the plate losses for experiments 11 and 12, in which apparatus Type II was used. While the results do not check exactly, they are more consistent than those of the previous experiments. The indications from the experiments of series I and II are that a current of 0.4 milliamps. per square inch (0.06 per sq. cm.) (figuring ⅓ of the back of the plate, as is customary) will prevent 93 to 94 percent of the corrosive action of N/10 H_2SO_4 in still water.

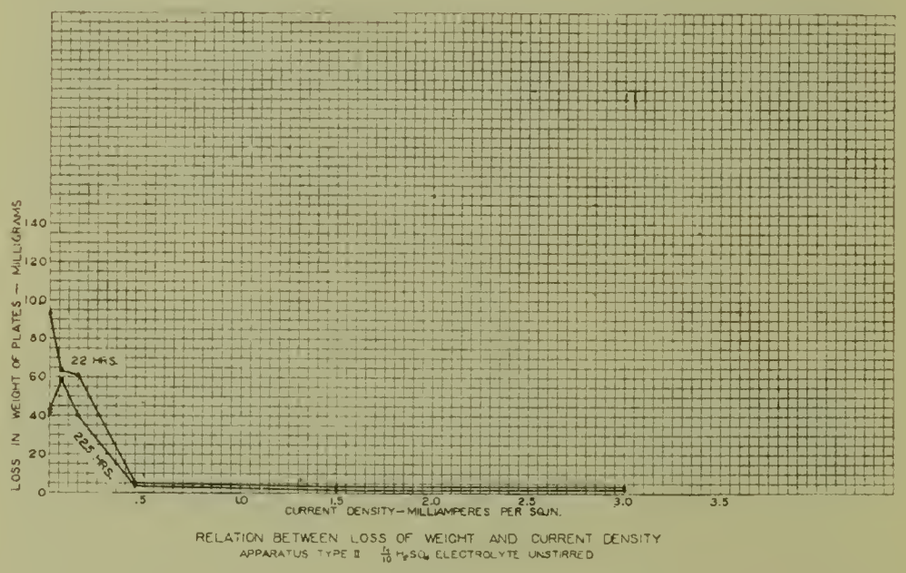


FIG. 4.

Experiments with Apparatus Type III.

The apparatus finally adopted, Type III, is shown in Fig. 5. It differs from Type II chiefly in having a greater capacity, 4½ liters, and in being provided with an attachment for stirring the electrolyte. The plates were arranged as before, except that they were set 2½ in. (6 cm.) from the carbon rod instead of 2 in. (5 cm.), in order to keep them under water when the electrolyte was rotating rapidly. For stirring, a low-power hot-air engine gave fairly constant speed and could be run over night. In order to be able to calculate our current densities with greater accuracy, all surfaces of the plates except the one facing the anode were protected by painting with Bakelite lacquer. An

application of four or five coats gave a good, smooth surface impenetrable to acids.

The first few experiments using the final apparatus were run with the stirrer rotating at 660 R. P. M., and, under these conditions, currents that had protected the iron plates almost completely in still water were absolutely useless. On cutting down the stirring rate to 35 R. P. M. in N/100 acid, small currents were again effective and runs could be checked with a fair degree of accuracy.

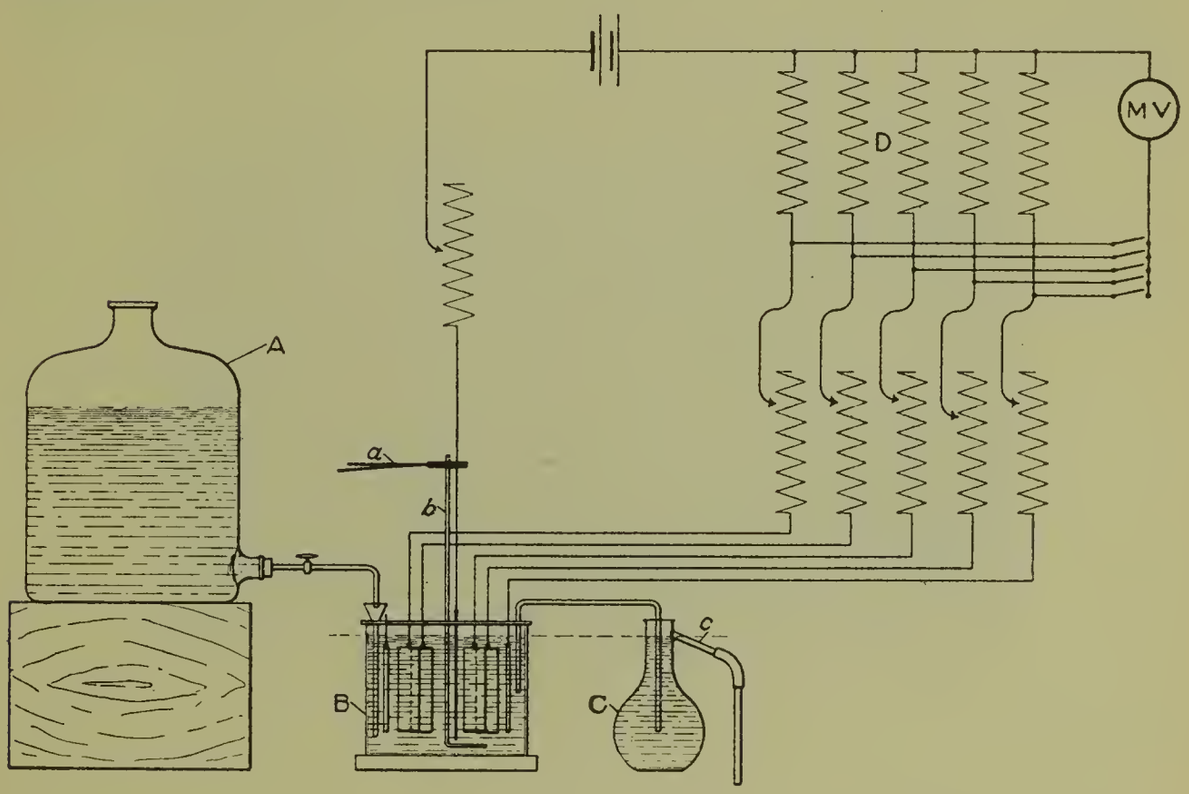
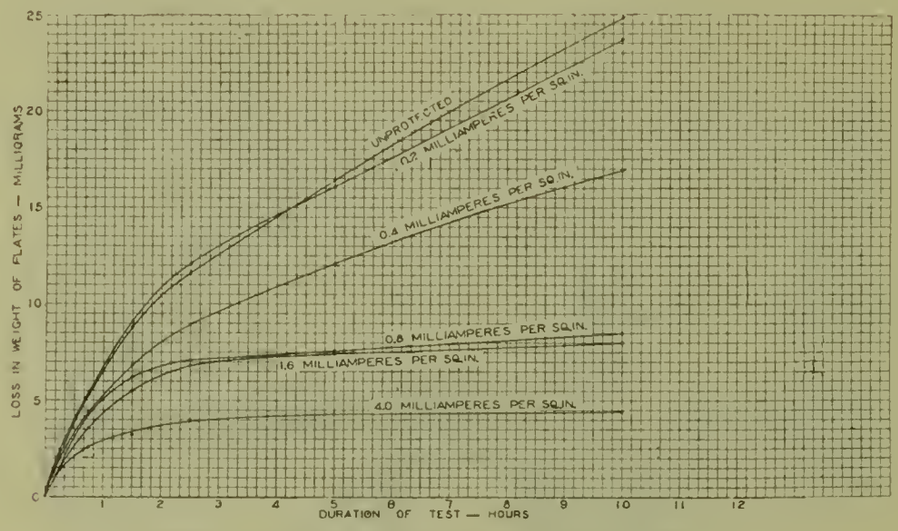


FIG. 5.

Fig. 6 shows the results of experiments using N/100 H_2SO_4 as electrolyte and with the stirrer running at 35 to 40 revolutions per minute. In this series of experiments the electrodes were removed from the electrolyte and their loss in weight determined at frequent intervals. The curves in Fig. 6 show that the plates having a current density of 0.4 milliampere per square inch (0.06 per sq. cm.) or less continued to lose weight during the entire period of the experiments. Plates protected by current densities greater than 0.4 milliampere per square inch exhibited a marked initial corrosion, and thereafter no further loss in weight. The initial loss in weight of the plates protected by current densities greater than 0.4 milliampere is probably due to

the fact that at the start of the experiment the plates were covered by a film of air, and that the oxygen of the air film acted as a depolarizer. Some time elapsed, therefore, before the plates became completely polarized, and during this period they were only partially protected by the current. The difference between the rate of loss in weight of the unprotected plate during the initial period and the rate during the remainder of the experiment is probably due to a difference in the structure of the original surface of the metal and that of the interior portion, as well as to the action of the film of air surrounding it at the beginning of the experiment.


LOSS IN WEIGHT OF PLATES — MILLIGRAMS
DURATION OF TEST — HOURS
UNPROTECTED
0.2 MILLIAMPERES PER SQ.IN.
0.4 MILLIAMPERES PER SQ.IN.
0.8 MILLIAMPERES PER SQ.IN.
1.6 MILLIAMPERES PER SQ.IN.
4.0 MILLIAMPERES PER SQ.IN.

EFFECT OF CURRENT DENSITY ON RELATION BETWEEN LOSS OF WEIGHT AND DURATION OF TEST.
APPARATUS, TYPE II $\frac{N}{100}$ H_2SO_4 ELECTROLYTE STIRRED, 35 R.P.M.

FIG. 6.

Effect of Passing Oxygen Through Electrolyte.

On account of the depolarizing effect of oxygen it was to be expected that the amount of oxygen present in the electrolyte would be an important factor in determining the speed of corrosion. Fig. 7 shows the results of a series of four experiments made to ascertain the effect of increasing the amount of oxygen in the electrolyte. The composition of the electrolyte and the speed of the stirrer were the same in all four experiments, *viz.*, N/100 H_2SO_4 and 35 R. P. M. The lower curves represent two experiments with the usual amount of oxygen present. The electrolyte was prepared by adding sulphuric acid to distilled water without any special precautions either to exclude the air or to aerate the solution. In experiments 38 and 39, represented by

the two upper curves, the electrolyte was saturated with oxygen by rapidly bubbling oxygen through the electrolyte during the experiment. The curves show that increasing the amount of oxygen in the solution accelerates the speed of corrosion very materially, the loss of weight in 24 hours being about twice as great when oxygen is passed through the electrolyte as when oxygen is supplied by diffusion only. It follows from this that the rate of corrosion in any acid solution will depend on the amount of aeration to which the solution is subjected.

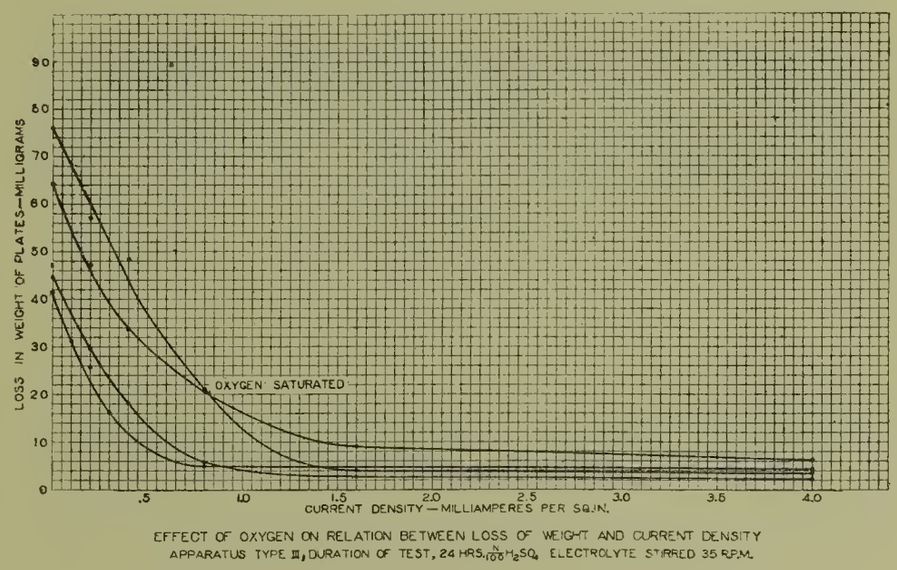


FIG. 7.

Effect of Stirring.

The enormous acceleration of corrosion produced by extremely rapid stirring, 660 R. P. M., has been noted above. On account of the magnitude of this effect a series of experiments was made in which the speed of the stirrer was the only variable. The results are shown in Fig. 8. An examination of the curves shows that, other conditions being constant, the loss in weight by corrosion varies directly as the rate of stirring. The increase in the speed of corrosion with the increase in the rate of stirring is further illustrated by Fig. 9, in which the loss in weight of the plates for several different current densities is plotted against the number of revolutions of the stirrer per minute.

These results demonstrate that the rate of flow of acid solution over the metal surface is an important factor in determining

the amount of corrosion and the current density necessary to protect the metal. The very considerable increase in the speed of corrosion produced by circulation of the electrolyte is not sur-

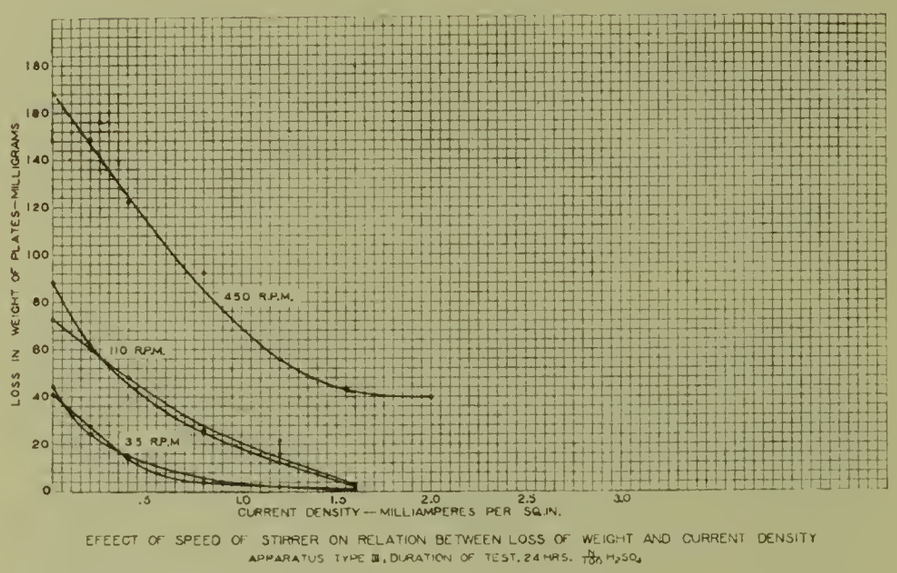


FIG. 8.

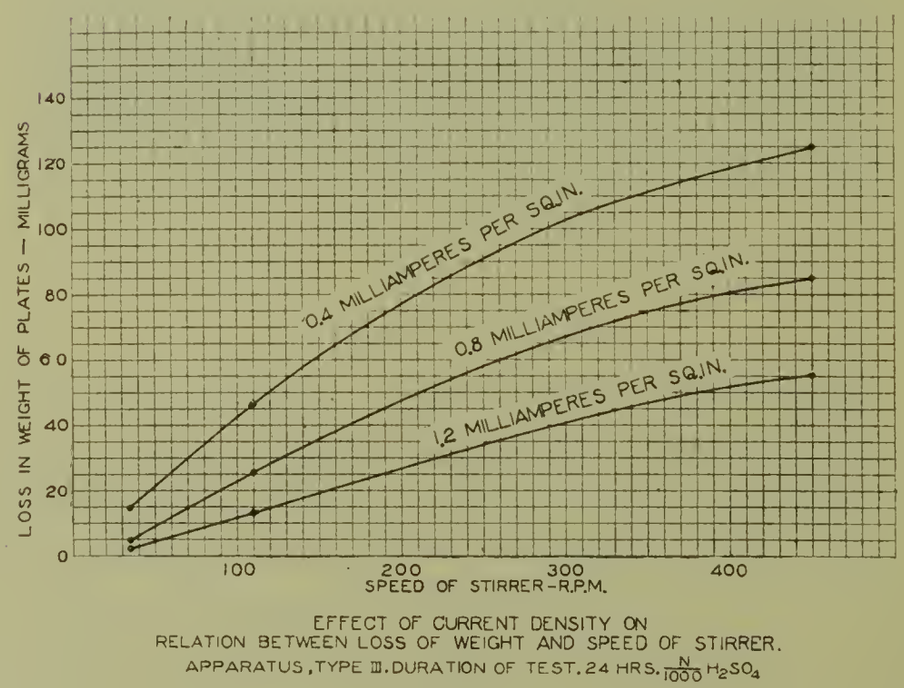
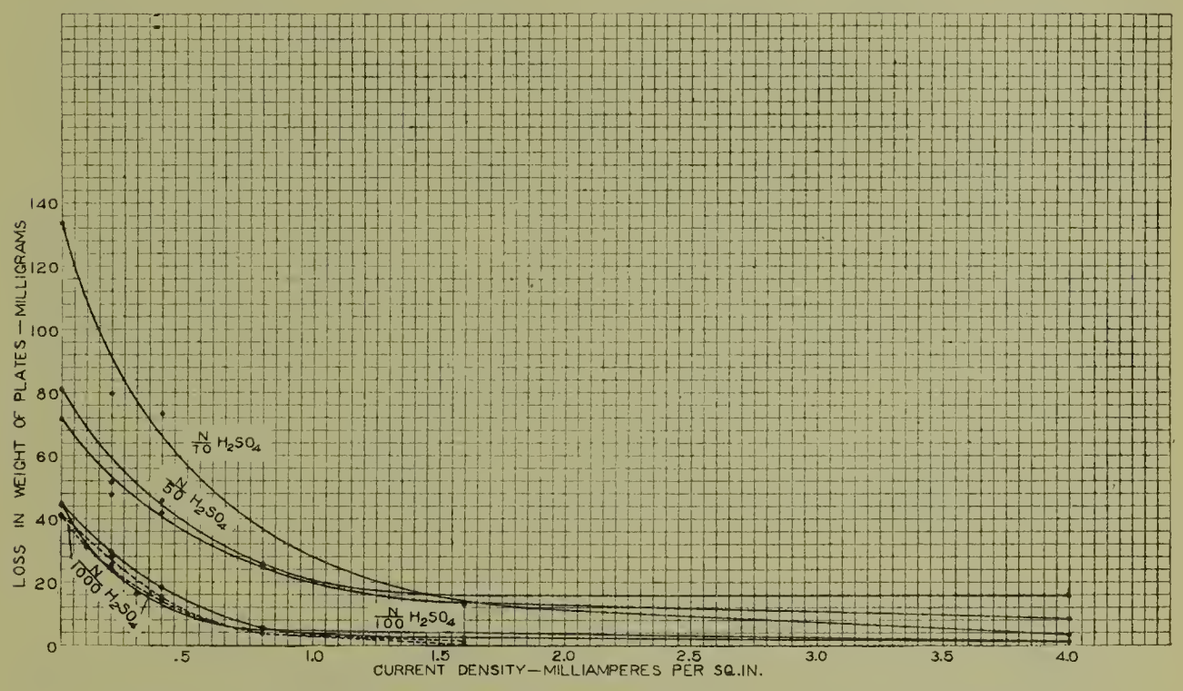


FIG. 9.

prising, since the flow of solution over the metal not only hinders the exhaustion of hydrogen ions in the vicinity of the anode, but provides a continual supply of oxygen and tends to destroy any film of hydrogen which may form on the surface of the cathode.

Acid Concentration.

That the rate of corrosion of iron or steel in sulphuric acid solutions increases with the acid concentration is well known. While the acid concentration in the natural waters in which the corrosion of iron ordinarily occurs is much below 1/100 normal, the concentration used in most of the experiments described, the application of the method to more concentrated solutions seemed of sufficient interest to justify experiments with stronger solutions. Accordingly a series of experiments was



EFFECT OF ACID CONCENTRATION UPON RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY.
APPARATUS TYPE III. DURATION OF TEST, 24 HRS. ELECTROLYTE STIRRED 35 R.P.M.

FIG. 10.

made in which the concentration of sulphuric acid was varied from 1/1000 normal to 1/10 normal. The results are represented by the curves in Fig. 10. They indicate that although a considerably greater current density would be required, the method would be effectual even in N/10 H_2SO_4. The curves for experiments with 1/100 normal and 1/1000 normal acid are practically identical, showing that between those limits of acid concentration there is no change in the rate of corrosion greater than the limit of error of observation. This result, though unexpected, was confirmed by repeated experiments.

Potential of Iron Electrodes.

In the majority of the experiments, in addition to measuring the current flowing into the different electrodes, the potential of the individual electrodes was measured against a zinc electrode. Potential readings were made with a Siemens & Halske millivoltmeter of 450 ohms resistance in series with a resistance of 17,550 ohms. The results are given in Table I. The agreement between the potentials of electrodes having the same current density is only fair. In N/100 H_2SO_4, and with a rate of stirring of 35 R.P.M., a current density of 0.8 milliampere per square inch (0.12 per sq. cm.) generally produced an increase in the potential of the iron electrode of about 0.04 volt. (In the table, potential differences are positive when the potential of the protected plate is positive to the unprotected plate, *i. e.*, when the potential difference between the zinc electrode and the protected plate is decreased by the protecting current.) As small an increase in the potential of the test plates as 0.04 volt sufficed, therefore, to protect them against corrosion. This effect is too small, especially in view of the variations found between the results of different experiments made under like conditions of acid concentration and rate of stirring, to be of value as a measure of the degree of protection against corrosion offered by the current.

Current Density.

In the experiments which have been described the following factors were found to influence the current density required to protect the corrosion of steel plates submerged in sulphuric acid solutions:

(a) Rate of stirring of electrolyte.

(b) Amount of oxygen present.

(c) Acid concentration.

Of these, the last named is probably of least importance, especially in dilute solutions.

The rate of stirring of the electrolyte is by far the most important factor. In practice the supply of oxygen in the immediate vicinity of submerged metal surfaces depends largely on the rate of flow of solution over the metal surface.

With the lowest rate of stirring used in the experiments, 35

R. P. M., and in acid concentrations not greater than 1/100 normal, a current density of from 0.5 to 0.8 milliampere per sq. in. (0.08 to 0.12 per sq. cm.) reduces the corrosion loss to a negligible quantity, while with the stirrer rotating at a speed of 450 R. P. M., and a current density of 2.0 milliamperes per sq. in. (0.3 per sq. cm.), the corrosion loss amounted to 25 percent of the loss on the unprotected plate.

Harker's Experiments.

From his experiments referred to above, Harker concluded that in employing the electrolytic process the current required to prevent corrosion might be calculated from the rate of corrosion of iron or steel under the given conditions and the electrochemical equivalent of iron. This he confirmed by one set of experiments in which, however, iron anodes were used. In experiments with a platinum anode Harker found that the protection afforded by the current to the iron cathode was somewhat less than when an iron anode was used. He concludes "that the electrolytic process does not actually prevent metal from entering the solution from the cathode, for, where the rate remains constant, deposition is taking place from the anode, yet the tendency of the metal to pass into solution is much diminished."

Application of Harker's Rule.

In all of the experiments made by the present authors a carbon anode was used. Harker's method of calculating the current density required to prevent corrosion was based on experiments with an iron anode. If, then, as Harker suggests, the protective action of the current is largely due to the transfer of iron from the anode to the cathode, it would not be expected that his method would hold for experiments with a carbon anode.

The method offers, however, such a simple procedure for arriving at the proper current density required to prevent corrosion that it seemed worth while to apply it to the results of the authors' experiments. In Table II are given the results of the authors' experiments, to which have been added the values for the current densities calculated from the loss in weight of the unprotected plates and the electrochemical equivalent of iron.

The "observed" values for the current densities in column 6 were obtained graphically from the curves in Figs. 2, 3, 4, 7, 8 and 10. The agreement between the observed and calculated values is remarkably good. The differences are well within the experimental error.

It may, therefore, be concluded that Harker's method of calculating the current density required to prevent corrosion, from the loss in weight of the metal under the given conditions, is not limited to cases in which an anode of the same metal is used.

The Nature of the Action of the Electric Current.

Harker's view that the current does not actually prevent metal from entering the solution from the cathode, and that its protective action is due to the deposition of metal from the anode, is contradicted by the authors' experiments in which carbon anodes only were used. The action of the current is, then, to prevent the formation of ferrous ions at the cathode by increasing its negative charge. In the absence of any depolarizer, especially of dissolved oxygen, an infinitesimal current should produce an electromotive force large enough to neutralize the solution tension of the metal. When oxygen is present it combines with the hydrogen ions liberated at the cathode and hinders polarization. The supply of hydrogen ions furnished by the current must be equivalent to the supply of oxygen in the vicinity of the cathode before the solution tension of the cathode can be completely neutralized.

Conclusion.

It has been shown that the corrosion of iron submerged in sulphuric acid solutions may be prevented by imposing a counter E. M. F. The density of the current required to prevent corrosion depends on various factors: acid concentration, amount of dissolved oxygen, and degree of circulation of electrolyte. The influence of these factors has been studied, and curves have been given showing the current density necessary under various conditions. It has been found that the current density required can be calculated, within the limit of experimental error, from the loss in weight of the metal under the given conditions when not protected.

TABLE I.

Electrode Potentials.

Current	Current Density Milliamperes		Potential Difference between Protected Plate and Unprotected Plate								
	Per Sq. In.	Per Sq. Cm.	Exp. 30	Exp. 31	Exp. 32	Exp. 35	Exp. 36	Exp. 37	Exp. 38	Exp. 39	Exp. 40
0.50	0.2	0.03	0.021	.004	—.021	—.024	.004	.012	.027	—.005	—.004
1.00	0.4	0.06		—.003	—.012	.003	.022	.008	—.018	—.051	—.024
2.00	0.8	0.12	0.198	.025	.102	.078	.073	.044	.012	.000	.015
4.00	1.6	0.26	0.433	.114	.237	.186	.187	.108	.102	.81	.090
10.00	4.0	0.64	0.723	.289	.429	.372	.392	.304	.315	.295	.303

Rate of stirring = 35 R. P. M.
ACID = N/100 H_2SO_4

TABLE II.

Figure	Experiment	Acid Conc.	Stirrer R. P. M.	Length of Run Hours	Observed Current Density Milliamperes per Square Inch.	Calculated Current Density Milliamperes per Square Inch	Losses Milligrams Unprotected Plate	
2	4	N/5	...	45	3.0	2.2	344.6	
3	6	N/10	...	47	3.0	3.4	551.5	
3	7	N/10	...	20	3.0	2.0	140.5	Apparatus Type I
3	9	N/10	...	23.5	1.5	2.7	221.0	
3	8	N/10	...	22	1.5	2.0	151.5	
4	11	N/10	...	22.5	0.45	0.5	43.0	Apparatus Type II
4	12	N/10	...	22	0.45	1.2	93.5	
7	39	N/100 Oxygen Saturated	35	24	1.6	1.3	75.9	
7	38	"	35	24	1.6	1.0	64.3	
7	40	N/100	35	24	0.8	0.7	44.6	
7	30	N/100	35	24	0.8	0.7	41.4	
8	48	N/1000	450	24	2.0	2.7	170.0	Apparatus Type III
8	45	N/1000	110	24	1.6	1.4	88.3	
8	46	N/1000	110	24	1.6	1.2	72.8	
8	42	N/1000	35	24	0.8	0.7	44.5	
8	41	N/1000	35	24	0.8	0.6	41.0	
10	51	N/10	35	24	1.6	2.2	133.8	
10	49	N/50	35	24	1.2	1.1	71.3	
10	50	N/50	35	24	1.2	1.3	80.9	

U. S. Bureau of Mines,
Pittsburgh, Pa.

DISCUSSION.

MR. J. O. HANDY: Have any calculations been made, based on the amount and cost of electric current, in order to see whether, under any conditions, it would be practical to use the electric method of protecting iron and steel exposed to acid water?

DR. J. K. CLEMENT: Tests are now being made on large plates submerged in the Monongahela River at Braddock, Pa., and until these large-scale experiments have been completed we should prefer to make no statement as to the amount of electric power required. In the laboratory experiments which have been described a current density of from 0.5 to 1.0 milliampere per square inch (0.08 to 0.15 milliampere per square centimeter) or 0.072 to 0.144 ampere per square foot (0.8 to 1.5 ampere per square meter) was usually sufficient to prevent corrosion. As the voltage required is low—it may be less than 1 volt when an iron anode is used—the cost of electric current, as indicated by the laboratory experiments, would be small enough to warrant the practical application of the electrolytic method

A paper presented at a Joint Session of Section Xa: Electrochemistry and Ve: Paints and Pigments, of the VIII International Congress of Applied Chemistry, in New York City, September 11, 1912.

THE INFLUENCE OF CINDERS ON THE CORROSION OF IRON IMBEDDED IN CLAY.

By Walter B. Schulte.

Investigations of electrolytic corrosion of underground structures occasionally reveal examples of marked corrosion under certain conditions which preclude a consideration of stray currents from electric railways as the cause. Filled ground seems to be especially harmful to iron pipes, especially where the filling is composed largely of cinders, coal, and furnace products.

Of the various explanations which have been offered to account for this corrosion, the more common are that the sulphur, which is a constituent of most coals, probably forms sulphuric acid, with the resultant chemical corrosion; also that cinders and particles of conductive carbon in contact with iron produce a local couple, and the pits which are formed are attributed to this effect.

The objection to the former theory is that the high temperature of burning usually expels the sulphur from the cinder material; and that the latter explanation is not completely adequate is indicated by the fact that the corrosion occurs even where there may be an intermediate layer of clay between the cinder bed and the pipe. Certain cases of deep pitting of iron pipe have been called to the attention of the writer where an overlying bed of cinder filling out of direct contact with the pipe seemed to be in a measure responsible for the damage noted.

It is well known that if a mass of carbon and a mass of iron are imbedded in an electrolytic conductor, such as in moist earth, a difference of potential is established between these two bodies, the iron being electrochemically positive to the carbon. This potential does not establish a flow of current unless metallic contact is made between these two bodies. While a layer of carbon material may be separated from an iron pipe in one locality by a

bed of sand or clay, corrosion may be produced at that locality by reason of contact between the iron and the carbon bed at some other position, such, for example, as occurs where a service pipe or other portion of the underground system may pass through the carbon bed. It is evident, therefore, that contact between the cinders and the iron is not necessary at the exact location where the corrosion is observed in order to account for such corrosion.

An active couple produced by carbon and iron results in the iron being the anode and the carbon being the cathode. Polarization tends to reduce the flow of current, but this polarization is minimized if air has ready access to the carbon bed; therefore the nearness of the carbon bed to the surface of the earth is a factor which influences the corrosion caused by such material.

The object of the investigation here described was to reproduce in the laboratory conditions which were found in the field, and to make laboratory measurements of potential and current flow and determination of the amount of corrosion. The experiments were carried out in the Chemical Engineering Laboratories of the University of Wisconsin.

Apparatus.

The apparatus as set up in the laboratory included a sheet of iron, buried in a bed of clay, on the top of which rested a layer of granular graphite, which represented the cinder bed. Electrical contact between the plate and cinders was provided for by a wire connecting them. The arrangement of the apparatus is shown in Fig. 1.

It is, of course, evident that the conductive layer of carbon here used has a higher electrical conductivity than that produced by cinder filling, as found in practice; and the reason for using this was to accelerate the action so as to produce measurable results within a short time.

The iron plate was of No. 24 sheet iron, pickled, dried and weighed before being placed in the clay, which was taken from a fresh excavation and was moist when placed in the box. The layers below and above the plate were well tamped in place. The carbon, which had been used as a resistor in electric furnaces,

was granular, the particles ranging from ¼ to ½ inch (6 to 12 mm.) in diameter. A graphite block with a stem was placed in the carbon to make electrical contact between the carbon and external connections, and insulated wire connected to the plate was brought out through the clay. The carbon lead was connected to a switch also connected to the iron plate terminal, so that by closing it the cell was short-circuited. The switch was provided with short leads, so that an ammeter or voltmeter could

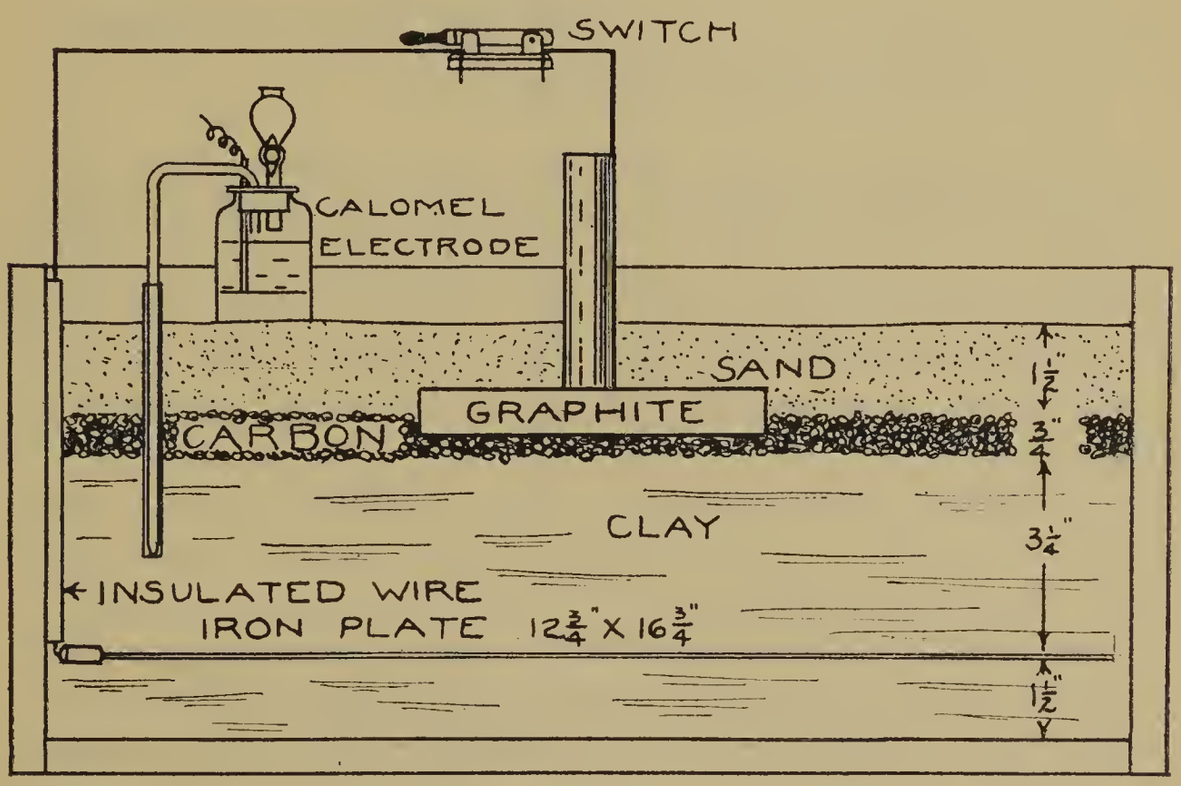


FIG. 1.

be connected to them and measurements be made with the switch open. The carbon was covered by a ½-inch (12 mm.) layer of sand at the beginning of the test, but this was removed on the fourth day.

To measure the single potentials of the iron and carbon against the clay a calomel electrode was employed, with a long nose reaching down through a glass tube into the clay half way between the carbon and iron. A few drops of normal KCl were poured into the bottom of the glass tube to moisten the clay and assure good contact between the clay and electrode.

Measurements.

Before closing the switch the potentials of the iron and carbon against the clay were determined by the potentiometer method, taking —0.56 volt as the potential of the calomel electrode. The results are given below:

Total E. M. F.	0.842 volt, carbon cathode
Clay to carbon	—0.638 volt
Iron to clay	+0.204 volt
Total	0.842 volt

A voltmeter indicated 0.83 volt.

After making the single potential measurements the circuit was inadvertently closed for a minute or two, after which the voltage, as indicated by a voltmeter, had fallen to 0.72 volt. Further short-circuiting caused the voltage to drop from 0.68 to between 0.45 and 0.50 after a few minutes. One and one-half minutes after opening the switch the voltage increased to 0.68 volt.

The cell was short-circuited for twenty minutes and the switch then opened, after which single potential measurements were made at various intervals.

After being on short-circuit for seventeen hours, similar single potential measurements were made, during which time the average current, as measured by a milliammeter, was 0.0515 ampere. The data of these measurements, as tabulated in Table I and plotted in Fig. 2, show that the rate of depolarization is decreased after the cell has been short-circuited for the longer time.

The cell was then allowed to stand short-circuited, and readings were made of the voltage and current at various times and during the run, the results of which are tabulated in Table II. The instruments were of standard make and in good calibration and of the following scales and resistances:

Voltmeter	0-15 volts;	53.5 ohms resistance
Ammeter	0-500 milliamperes;	0.09 ohm resistance

During the fourth day the layer of sand above the carbon was removed, as noted in the table. The clay began to dry out, so that

beginning with the tenth day about half a liter of water was sprinkled over the carbon and allowed to soak in before a set of readings were made. No readings were taken between the thirty-third and fifty-eighth days, nor was the cell moistened, with the result that the current on the fifty-eighth day was almost nil, and the potential 0.22 volt. Three minutes after the cell had been moistened the observed values increased to 0.0175 ampere and 0.32 volt.

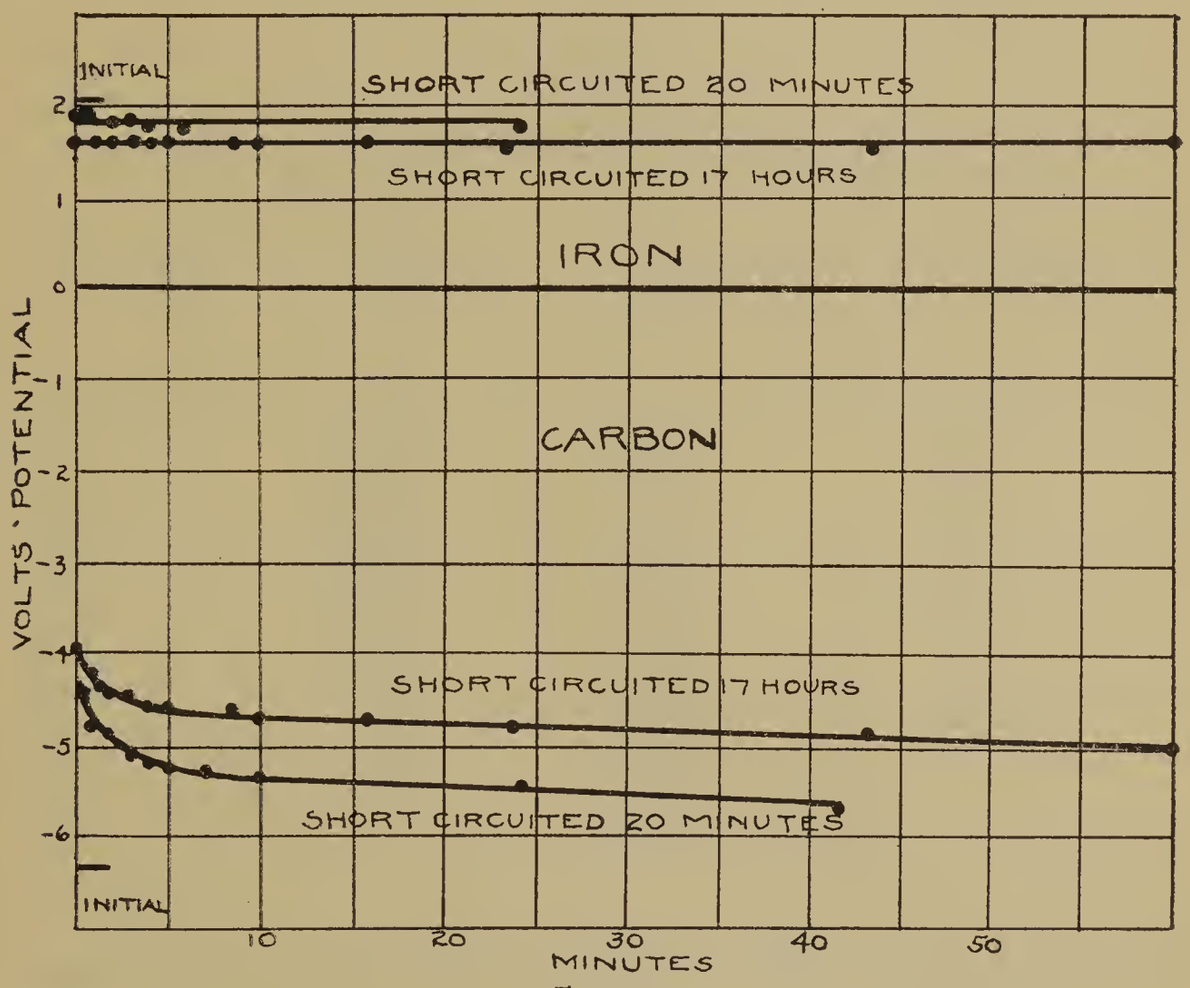


FIG. 2.

Rough integration of the curve plotted between current and days, with the current as zero on the fifty-eighth day, gives 35 ampere-hours. If the cell had been moistened regularly each day throughout the test it is fair to assume that the average current would have been 0.03 ampere; 0.03 ampere for 58 days is equivalent to about 42 ampere-hours. The average voltage over this period can be taken as 0.35 volt.

The interesting point to be noted is that as long as the clay was moist a current flowed continuously from the iron to the

carbon, the depolarization, due presumably to the action of the air on the carbon, taking place at a constant rate.

The corrosion of iron by one ampere-year is about 20 pounds, so that 0.03 ampere, the assumed average current with the clay moist, would corrode about $20 \times 0.03 = 0.6$ pound.

The area of the plate was 1.45 square feet (12 sq. dm.), or 2.9 square feet (24 sq. dm.) total surface, so that the theoretical corrosion per square foot would be 0.23 pound (12 grams per

TABLE I.

Depolarization.

Single Potentials of Carbon				Single Potentials of Iron			
Short-circuited 20 Minutes		Short-circuited 17 Hours		Short-circuited 20 Minutes		Short-circuited 17 Hours	
Time Min.	E. M. F.	Time Min.	E. M. F.	Time Min.	E. M. F.	Time Min.	E. M. F.
½	—0.432	0	—0.394	0	+0.184	0	+0.162
1	—0.478	1	—0.424	¼	+0.184	1	+0.160
2	—0.485	1½	—0.434	¾	+0.186	2	+0.160
3	—0.508	2	—0.438	2	+0.180	3	+0.160
4	—0.510	3	—0.442	3	+0.182	4	+0.160
5	—0.516	4	—0.452	4	+0.180	5	+0.160
7	—0.524	5	—0.452	6	+0.178	8	+0.158
10	—0.530	8	—0.458	24	+0.180	10	+0.158
24	—0.540	10	—0.468			16	+0.158
42	—0.564	16	—0.470			23	+0.156
		23	—0.474			43	+0.156
		43	—0.484			60	+0.158
		60	—0.499				

sq. dm.) per year. This loss, or about one-quarter pound, on a plate would destroy the equivalent of a No. 30 sheet in one year, or half of a No. 24 sheet. If this corrosion were concentrated in six square inches area on every square foot (on 4 percent of the surface), the metal would be pitted to the depth of 0.15 inch (4 mm.), which would pierce a 3-inch (75 mm.) cast iron main in a little over two and one-half years.

Corrosion of Plate.

After the fifty-eighth day the cell was dismantled. Examination of the clay near the plate showed that the rust had pene-

trated into it as much as ¼ inch (6 mm.) in some places. The plate was spotted with oxide and greenish iron compounds. Corrosion was noticed both on the upper and lower sides of the plate, and the corner diagonally opposite the wire connection was eaten through.

TABLE II.

Current and Voltage Readings.

Day	Amperes	Volts	Remarks
1	0.052	0.45	
2	0.0518	0.50	
3	0.050	0.45	
4	0.051	0.45	Sand removed from top
5	0.051	0.44	
7	0.0495	0.38	
8	0.035	0.40	
9	0.030	0.20	
10	0.040		Began wetting
11	0.035	0.40	
12	0.0475	0.42	
14	0.0475	0.42	
15	0.040	0.42	
17	0.041	0.40	
24	0.030	0.35	Dried out since last reading
25	0.0375	0.36	
29	0.023	0.30	
30	0.020	0.20	
31	0.035	0.40	
32	0.028	0.35	
33	0.028	0.35	
58	0.015	0.32	

The plate was washed, the greater part of the rust scraped off, and the remainder then dissolved off by hot ammonium citrate, after which it was weighed. The data follow:

Weight of plate before test..... 401.6 grams
Weight of plate after test..... 346.5 grams

Loss ..... 55.1 grams

Thirty-five ampere-hours theoretically would corrode 36.4 grams of iron so that the efficiency of corrosion in this case would be about 150 percent. That is, it may be said that two-thirds of the loss by corrosion was due to the current pro-

duced by the difference of potential between the carbon and the iron.

These experiments were intended as preliminary work for further investigation, which, however, was not undertaken; but a description of this first, rather incomplete work, it was thought, would prove of interest and draw attention to the influence of carbon and cinders on the corrosion of iron, and perhaps lead to further experimenting on the subject. Further work along this line should be undertaken with the conditions more closely approaching those actually found, that is, using cinders instead of carbon, and putting them, with the iron plate, in the earth. Similar plates not connected with the carbon should also be buried so that the amount of natural corrosion can be determined. Under these conditions, with the higher resistant cinders, it is to be expected that less current would be produced.

An interesting case of corrosion of a gas pipe, which may be explained by action similar to that discussed above, has been observed recently by the writer. Along a certain street the gas mains were paralleled by a water main buried a short distance beneath. The soil is mainly clay or silt, but at the lowest portion of the street the water main dipped into a peaty layer. The gas main lay in the clay above the peat at this point, and was corroded through at several places. The main apparently was in a locality not subjected to stray currents from the street railway or grounded power circuits, so that the currents causing the corrosion must have come from other sources.

A length of gas main about 400 feet long was disconnected from an adjoining portion. Potential measurements between this disconnected length and an iron rod driven in the black layer showed that the gas main was 0.3 volt positive, and readings between gas and water connections showed that current was flowing from the gas to the water main through the earth. The corrosion can be explained by the fact that peat sets up a different potential toward an iron surface than does clay, and connections between the gas and water services on the consumer's premises make the couple electrolytically active, thereby producing electrolytic corrosion.

Chemical Engineering Laboratories,
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DISCUSSION.

MR. J. O. HANDY: Has the composition of the cinder any influence? There is a greater amount of sulphur in some cinders than in others.

PROF. C. F. BURGESS: Of course a cinder body such as locomotive cinders and different furnace ashes has very poor conductivity. Sulphur does not seem to play any part.

MR. HANDY: I made some comparative corrosion experiments, having samples of different kinds of steel embedded in coke of a maximum size of a quarter of an inch and kept moist for a period of about three weeks. The pitting during that time was very marked.

A Paper read at a Joint Session of Sections Xa: Electrochemistry, and Ve: Paints, of the VIII International Congress of Applied Chemistry, in New York City, September 11, 1912. Dr. W. H. Walker in the Chair.

THE RATE OF RUSTING OF IRON AND STEEL

By James Aston and Charles F. Burgess.

An editorial review of chemical progress in 1911 says:[1]

"The rusting of iron has received its usual amount of study and controversy, but the question remains as ragged and dubious as it has been for years. Part of the difficulty arises from some of the investigators falling in love with a neat, trim, complete theory, blinding their eyes to its defects, and rejecting the contributions of other workers who do not worship their own idol."

In spite of the vast amount of study which has been given this subject, it is a regrettable fact that there is but a limited amount of information and data available bearing upon the practical phases of the question. The painstaking and detailed work which has been devoted to proving or disproving a theory that carbonic acid is the cause of rusting is illustrated by the fact that one of the prominent workers in this field asserts that in spite of boiling and other methods of purifying there still adhered to the inner walls of a glass vessel in which corrosion tests were made enough CO_2 from the glass blower's breath to make the results of tests of doubtful value. On the other hand the controversy on the intensely practical question as to the relative durability of iron and steel is still unsettled; there is no reliable information as to how durability is dependent upon purity and as to the quantitative influence of various impurities. There are no standard methods of testing, by means of which the corrosion determinations made by one investigator may be compared with those made by another.

For a number of years experimental work has been carried on in the Chemical Engineering Laboratories of the University of Wisconsin on various phases of iron corrosion, and the purpose of this paper is to present some of these results as far as

[1] The Engineer (London), Jan. 12, 1912.

they deal with commercial forms of iron and steel. Various grades of commercial materials were subjected to corrosion tests during 1910 and 1911, and in presenting these results the purpose is not to draw an accurate comparison of the relative merits of various commercial materials at present available, but rather to give some data on testing methods. In view of marked advances which have recently been made, the samples which were selected early in 1909 probably do not include representative samples of some of the high purity materials at present available.

No attempt is made to classify the results in accord with any theory, but rather to submit them in such manner that they may serve as a record containing some information of general usefulness, and to which results of further measurements which are under way may be compared.

While appreciating the limitations upon corrosion data as generally submitted, and while desiring to make our tests standard as far as possible, we must recognize serious limitations on our own results—limitations due partly to lack of foresight and partly to lack of facilities, time and financial resources.

Samples were prepared from six different classes of materials as representative of the range of materials obtainable on the market. These comprise several grades of open-hearth iron of high chemical purity, Swedish iron, open hearth mild steel, open hearth mild steel subjected to special hot working process, Bessemer rail steel, and gray cast iron. Some of these materials were chosen both from bar and sheet stock.

The list of materials thus chosen comprise twelve in number, and six samples of each were prepared for and subjected to various corrosion tests, there being 72 test specimens in all.

The twelve materials are described in the following list:

1. Open-hearth high purity iron from bar stock.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.) ground to smooth surface on emery disc.

2. Open-hearth high purity iron.—Samples 1 x 2 x ¼ in. (2.5 x 5 x 0.65 cm.) ground to smooth surface.

3. Open-hearth high purity iron.—Samples 3 x 3 in. (7.5 x 7.5 x 0.16 cm.) from 16 gauge sheet. Samples were used with black annealing scale.

4. Same as 3, but ground smooth on emery disc to remove scale.

5. Swedish wrought iron.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.) ground smooth.

6. Open-hearth steel—from plate stock.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.)—taken as representative of good quality low carbon steel of the better grade used in boiler plate.

7. Open-hearth steel sheet—16 gauge.—Samples 3 x 3 in. (7.5 x 7.5 x 0.16 cm.) with annealing scale. From designation by the manufacturer it is representative of very mild, annealed, high grade open hearth product.

8. Same as No. 7, but with scale removed and surface ground smooth.

9. Open-hearth special sheet steel, 20 gauge.—Samples 3 x 3 in. (7.5 x 7.5 x 0.1 cm.) with annealing scale. It is represented as a special steel, by reason of a mechanical treatment of the ingot during working down with the idea of eliminating surface heterogeneity and blow holes.

10. Same as No. 9, but with scale removed and surface ground smooth.

11. Bessemer steel.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.) cut from the flange of a steel rail. Analysis not determined, but may be taken as representative of material having carbon content of 0.50 to 0.60.

12. Cast iron.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.) cut from a medium-grained, gray-iron casting. Analysis not determined, but representative of average iron casting, except that the scale or surface chill has been removed.

Six samples of each of the above listed materials were subjected to tests for corrosion; these are indicated by *a, b, c, d, e,* and *f* respectively; *a, b* and *c* were exposed to the weather conditions on the roof of the Chemical Engineering building, at the University of Wisconsin, and *d, e* and *f* were placed at the ventilator outlet on the roof of the Chemistry Building, where together with the weathering conditions additional corrosive action was exerted by the gaseous fumes from the chemical laboratory. It is believed that in the former case we have typical atmospheric corrosive conditions uninfluenced by smoke and

fume, while in the latter case the atmospheric corrosion is considerably aggravated by fume. The former will be designated as "atmospheric corrosion," and the latter as "fume corrosion." The fume corrosion was not, however, excessively severe, since the ventilating fan discharged the heated air at a high velocity, with conditions favorable for the rapid drying of specimens after wetting from atmospheric conditions.

All samples were ground or polished to a uniformly smooth surface on a fine emery disc. However, with the sheet material, duplicate sets were exposed without removal of the rolling or annealing scale. The bar samples were set in wood racks, and the sheet samples suspended in frames, all edge up; the racks were built to allow for as good drainage as possible. All specimens were first exposed on December 22, 1910, after weighing. On March 8, 1911, one of each of the three making up the various sets was taken in, the rust removed by ammonium citrate solution, and the loss determined. These samples were then exposed (without altering the surface conditions) a second time, on March 8, 1911. On May 21, 1911, the above mentioned samples, together with one of each set which had been out for the total period from December 22, 1910 to May 21, 1911, were taken in, and the amount of corrosion determined.

All of these specimens were then ground to a smooth finish, weighed and subjected to 20 percent sulphuric acid corrosion for one hour, according to the specifications suggested by the American Society for Testing Materials. This loss was then determined. Finally, after regrinding and weighing, the bar samples were again exposed to the previous weathering conditions on June 1, 1911. The sheets were too much corroded by the acid to be available for this test. On October 18, 1911, all specimens, including three of each bar sample, and one of each sheet sample, were taken in and the corrosion loss determined.

At the completion of these tests, all of the bar samples, Nos. *1, 2, 5, 6, 11* and *12,* were examined as to character and depth of pitting. This character of pitting is shown photographically. The depth of pitting was determined by carefully grinding down one of the faces of each specimen, until the pit marks just disappeared, and the amount of metal thus removed was noted. To these values were added the losses by corrosion, and the sum

gives a value called for convenience the "equivalent corrosion" per square inch. Then by dividing the "equivalent corrosion" by the actual corrosion we have values which we choose to designate as the "pitting factor."

The diagram, Fig. 1, will illustrate perhaps somewhat more clearly the various steps through which each set of samples passed.

In making the acid tests at the end of the second period the average of *a* and *b* and of *d* and *e* were taken—it being found that close agreement existed between the two samples of each pair, though not between the two pairs.

DIAGRAM I.

	Atmospheric			*Fume*		
	a	*b*	*c*	*d*	*e*	*f*
Dec. 22, 1910:	.....	.....	.....	.....	.....	.....
March 8, 1911: End of 75 days—*a* and *d*, freed from rust—loss determined and replaced.						
May 21, 1911: End of 150 days—*a*, *b*, *d* and *e* had rust removed, loss determined and ground to smooth surface. Then subjected to acid test. Then ground again to smooth surface, and exposed for 139 days.						
June 1, 1911:	.....	.....	.....	.....	.....	.....
Oct. 18, 1911: End of 300 days—all samples taken in and loss determined.						

From analysis of the data thus obtained certain conclusions of interest and of possible value may be drawn as having a bearing upon the important problem of corrosion. The question which is perhaps of the greatest importance and of interest to the greatest number is "What is the relative durability of the various materials on the market under various corrosive conditions?" This is a question which we do not attempt to answer. Although some of the tables presented herein appear to give numerical expression to the corrodibility of various grades of materials, they cannot be used as a guide, since it is by no means certain that the small samples employed were truly representative of the classes of materials from which they were drawn. In

fact, recent microscopic analysis seems to show that in one instance at least especially inferior samples were employed in these tests. However, it is believed that the figures represent some concrete idea of the possible ranges of values which may be encountered in commercial materials as judged from the durability standpoint.

Other and more reliable conclusions can be drawn from these tests. It is shown that atmospheric corrosion depends upon the seasons of the year and upon the gaseous impurities in the air; that these impurities affect different grades of iron and steel in different degrees. Much interest attaches at the present time to the usefulness of the accelerated acid test as a means of judging the durability of the metal under various corrosive conditions, and some conclusive evidence is given to show that there is little relationship. The accelerating influence of an initial rust formation upon subsequent rusting is demonstrated. The black scale on sheet iron is shown to have little, if any, retarding influence upon deterioration by rusting. A peculiarity is apparently pointed out that iron after exposure to severe atmospheric corrosive conditions undergoes some deep-seated change, which is evidenced by a notably decreased resistance to attack by acid. It is well known that the damage to iron by rusting is not measurable alone by the loss of weight of the metal, but the depth of pitting produced by the rust is an important factor. An attempt is made to give a numerical expression to this factor.

In Tables I and II the results are given as "corrosion factors," the reference unit being taken as the rate at which material No. 1 rusted per day under normal atmospheric exposure during the winter period. The use of the "corrosion factor" is in accordance with the practice recommended by Friend.[2] In making measurements, all of the corrosion losses were reduced to loss per square inch per day, and the ratio of that loss compared with the sample chosen as standard constitutes the corrosion factors. In order that these corrosion factors can be converted into actual loss of weight per day, there is given the "corrosion constant," which is 0.00092 g. per sq. inch per day, or 0.01426 g. per sq. dcm.

[2] The Corrosion of Iron and Steel, J. Newton Friend, p. 276.

Table I is of greater practical importance, since the "fume test" represents only a special artificial condition not capable of reproduction.

The influence of the seasons upon corrodibility is marked. The average of the corrosion factors of the twelve materials for winter is 118, for the spring 169, and for the summer and autumn 60.

TABLE I.

Material	Corrosion Factors: Atmospheric Test (a) 1st Period 75 days Winter	(a) 2nd Period 75 days Spring	(b) Combined Period of 150 days	(a) 139 day Period Summer	(b) 139 day Period Summer	(c) Total Period of 300 days
1. High purity iron ½" bar	100	134	154	74	79	79.6
2. High purity iron ¼" bar	94.5	100	143	67	59	83.2
3. High purity iron sheet with scale	148	135	149	..	..	109
4. High purity iron sheet without scale	124	124	135	..	..	90.5
5. Swedish iron ½" bar	82.5	96	141	48.5	73.5	73.5
6. Open hearth steel boiler plate	97	123	135	48.5	51	99
7. Open hearth steel sheet with scale	141	193	177	..	..	186
8. Open hearth steel sheet without scale	169	175	185	..	..	150
9. Special sheet steel with scale	121	460	307	..	..	160
10. Special sheet steel without scale	137	276	254	..	..	149
11. Bessemer rail steel	91	95	123	51	59	63.5
12. Gray cast iron	113	105	91.5	59	54	93

Corrosion constant = 100 = 0.00092 g. pr. sq. in. per day = 0.01426 g. sq. dcm.

It is unfortunate that the tests did not cover a 365 day run—but the figures given in the 300 day column may be taken as representing approximately the behavior of the metals when exposed to a year's atmospheric attack. The average 300 day corrosion factor is 111. The corrosion constant being 0.01426 g. per sq. dcm. per day, the amount of corrosion per year is 365 x 1.11 x 0.01426 = 5.777 g. per sq. dcm. of surface per year.

Assuming a uniform corrosion without pitting, the thickness of iron removed by rust per year would be according to the

above figure, and with the specific gravity of iron taken as eight, 0.00722 cm. or 0.00284 inch.

On this basis a 16-gauge sheet, having a thickness of 1/16 in. (0.16 cm.) when exposed to atmospheric corrosion on both sides, would have a life of 11 years. This is a longer life than would actually be attained, because of pitting and other disturbing factors. It is, of course, not demonstrated by these tests whether there is an accelerating or retarding action during succeeding years.

TABLE II.

Material	Corrosion Factors (d) 1st Period 75 days	(d) 2nd Period 75 days	(e) Combined Period 150 days	Fume Test (d) 139 day Period Summer	(e) 139 day Period Summer	(f) Total Period 300 days
1. High purity iron ½" bar...	147	305	211	134	132	189
2. High purity iron ¼" bar..	146	325	207	117	108	183
3. High purity iron sheet with scale	157	305	193	...	...	160
4. High purity iron sheet without scale	128	299	200	...	...	216
5. Swedish iron ½" bar.....	133	244	144	88.5	95	122
6. Open hearth steel boiler plate	138	251	179	107	124	111
7. Open hearth steel sheet with scale	116	280	134	...	...	108
8. Open hearth steel sheet without scale	163	337	377	...	...	148
9. Special sheet steel with scale	185	303	250	...	...	161
10. Special sheet steel without scale	173	307	340	...	...	135
11. Bessemer rail steel	97	140	87	93.5	83	63.5
12. Gray cast iron	117	150	115	73.5	83	67.2

Corrosion constant = 100 = 0.00092 g. pr. sq. in. per day = 0.01426 g. sq. dcm. per day.

As to the relative durabiltiy of different grades of materials, no absolute conclusions are possible, since the samples chosen may not be truly representative, but on the assumption that they are, we have a range from 63.5, as representing the most resistant, to 186 for the least resistant, or a variation of over one hundred percent.

That a commercial material, even though it may be of a uniform and constant composition and structure, cannot be assigned

a definite "corrosion factor" is shown by comparison of Table I with Table II. The more resistant metals under atmospheric corrosion become the less resistant under another kind of corrosive atmosphere. That is, the corrosion conditions are important as affecting the relative durability of a given list of materials. Following this line, then, the "atmospheric" corrosion to which these samples were subjected is not necessarily the same as atmospheric corrosion in other sections of the country, and the data obtained cannot be used therefore without reservation.

TABLE III.

Acid Corrosion.—Relative Losses by Standard Acid Test.

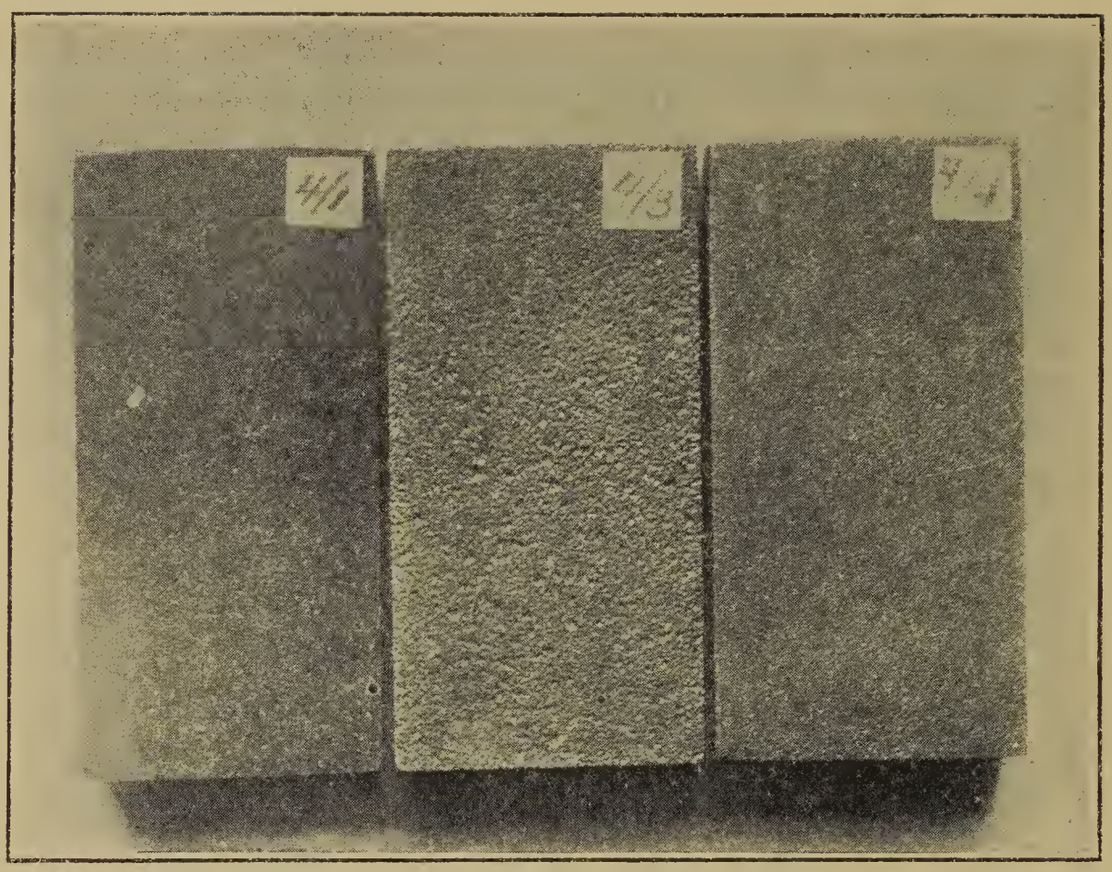
	(*A*) Samples first exposed to atmospheric corrosion	(*B*) Samples first exposed to fume corrosion	B/A
1	100	140	1.40
2	79	142	1.80
3	67	168	2.54
4	80.5	136	1.69
5	320	361	1.13
6	1,960	2,210	1.13
7	5,500	9,000	1.63
8	5,150	11,500	2.24
9	6,710	7,050	1.05
10	7,770	4,450	0.57
11	2,100	3,170	1.51
12	3,330	4,080	1.23

Corrosion constant = 100 = 0.0072 gr. per sq inch surface per hour = 0.00115 gr. per sq. cm. per hour.

Acid Corrosion.

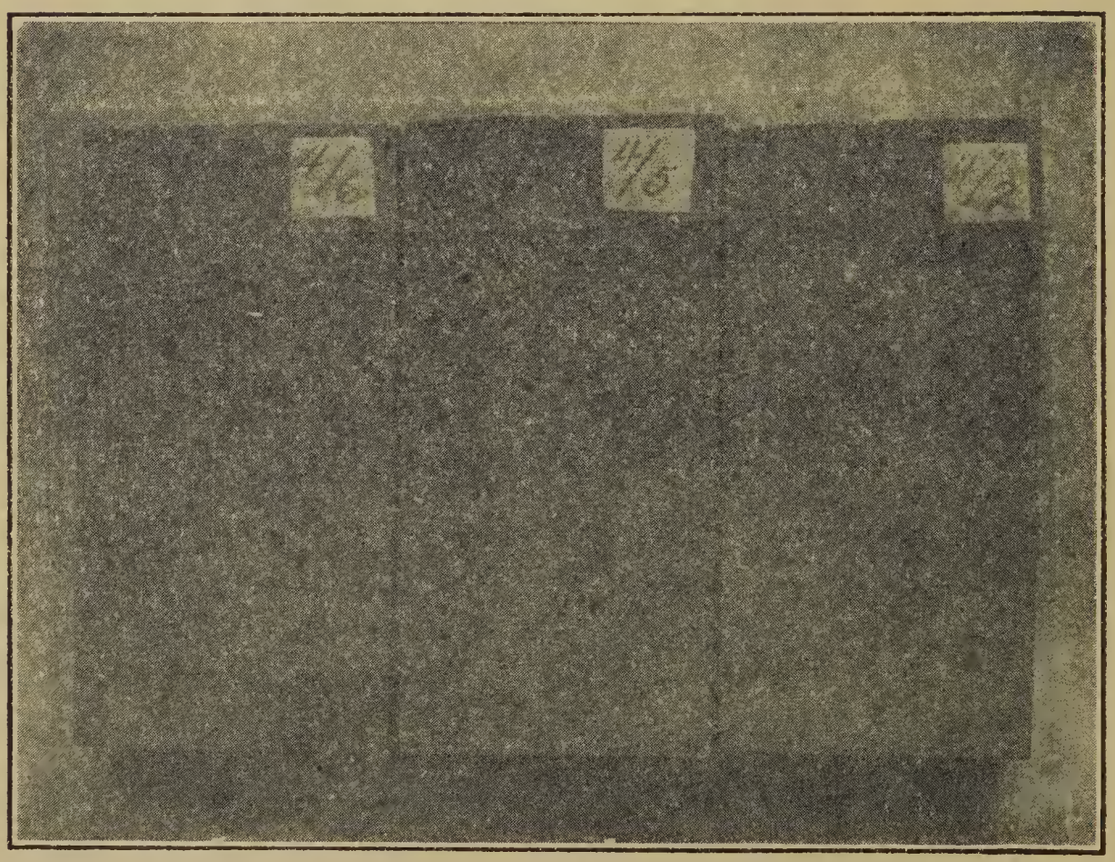
After having been exposed to atmospheric and fume corrosion for 150 days, the samples were ground down to a smooth, bright surface and exposed to the standard sulphuric acid test. There were duplicate samples of each material, and the results recorded in Table III are the averages of these two determinations. That there were only very small errors in measurement was shown by the close agreement between the losses of each of the two corresponding samples.

By comparison of the last column of Table I, giving corrosion factors for atmospheric corrosion, with the first column of Table III, giving the corrosion factors for acid corrosion, we had a



139 Days. 300 days. 139 days.

FIG. 2. Atmospheric Corrosion, Open Hearth Steel Plate.



139 Days. 300 Days. 139 Days.

FIG. 3. Fume Corrosion, Open Hearth Steel Plate.

means of judging something of the significance of the acid test. There is seen to be no direct relationship between the two tests. The four materials showing the highest acid corrosion were the ones showing the highest rate of atmospheric corrosion, but the sample showing the least atmospheric corrosion, the Bessemer rail material, has a high acid corrosion rate. While the high purity samples had the lowest rates of acid corrosion, and were likewise below the average in rate of atmospheric rusting, there is no direct relationship as between the respective samples of this class of materials.

TABLE IV.

Influence of Scale on Rate of Rusting.

Atmospheric Test.

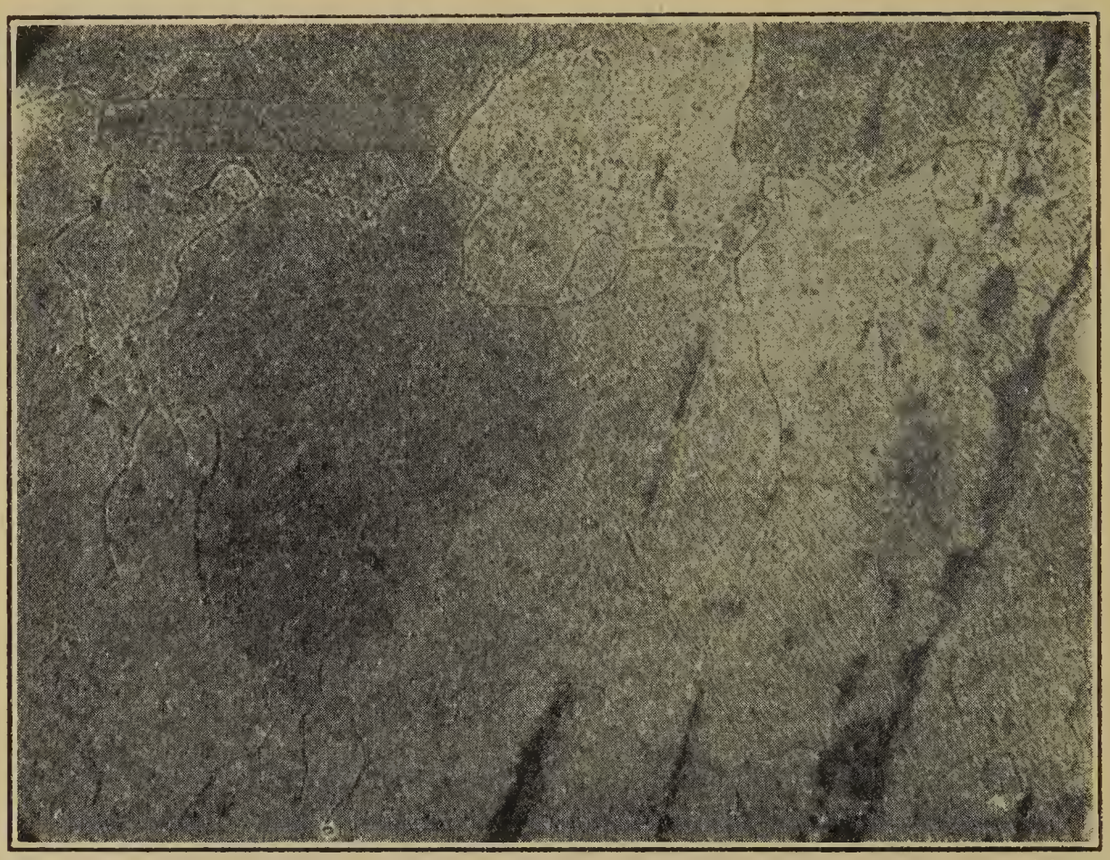
Material	75 day Period		150 day Period		300 day Period	
	with scale	without scale	with scale	without scale	with scale	without scale
3 and *4*— High purity iron..	148	124	149	135	109	90.5
7 and *8*— Open hearth mild steel	141	169	177	185	186	150
9 and *10*— Open hearth special steel	121	137	307	254	160	149
Totals	410	430	633	574	455	389.5

Fume Test.

3 and *4*— High purity iron..	157	128	193	200	160	216
7 and *8*— Open hearth mild steel	116	163	134	377	108	148
9 and *10*— Open hearth special steel	185	173	256	340	161	135
Totals	458	464	583	917	429	499

By comparison of the acid corrosion with the fume corrosion tests, column 2 of Table III and column 6 of Table II, there is seen to be no utility in the acid test, since the samples most resistant to acid were among the least resistant to the fumes.

A characteristic of the acid test is its extreme sensitiveness,



× 70

FIG. 4. Low Carbon Areas with Slag.

× 70

FIG. 5. Medium Carbon Area with Slag.

the most corrodible metal being dissolved 116 times as rapidly as the most resistant. The atmospheric test shows a ratio of only 2.9 as between the most and the least corrosive. Evidently there are factors which influence the rate of acid attack which do not enter into atmospheric corrosion.

An interesting phenomenon is shown in column three of the acid corrosion table, in that the attack on the metals which had been subjected to fume corrosion was notably greater, with but one exception, than on those which had been subjected to atmospheric attack. Just why this should be is not evident, but it appears that the fume corrosion has had a deep-seated action, penetrating into the metal and making it more susceptible to acid corrosion.

Influence of Scale on Rate of Rusting.

In making quantitative corrosion determinations, and a comparison of durability of different classes of material, the question arises as to the influence of the black scale which comes on commercial sheet, and whether for sake of comparison it is important that all of this scale be removed before beginning a test. This in turn depends upon whether the oxide scale has a protective or accelerating action. There is no doubt that the protective property of mill scale is dependent upon its physical properties, continuity, etc.

It was the purpose in conducting these tests to make comparison of rusting on samples identical in every particular except as to presence of the mill scale. In the above tables, materials Nos. *3, 4, 7, 8, 9, 10,* were subjected to this comparison, the odd numbered materials being tested with the scale, while from the even numbered materials the scale was carefully removed by mechanical means before the test.

The results of this comparison are presented in Table IV.

Except for the first 75-day period it is shown that the mill scale had an accelerating effect for the atmospheric test and a retardent action for the fume test.

Accelerating Influence of Rust.

It is a generally accepted belief that rust having once formed upon an iron surface, this adhering rust exerts an accelerating

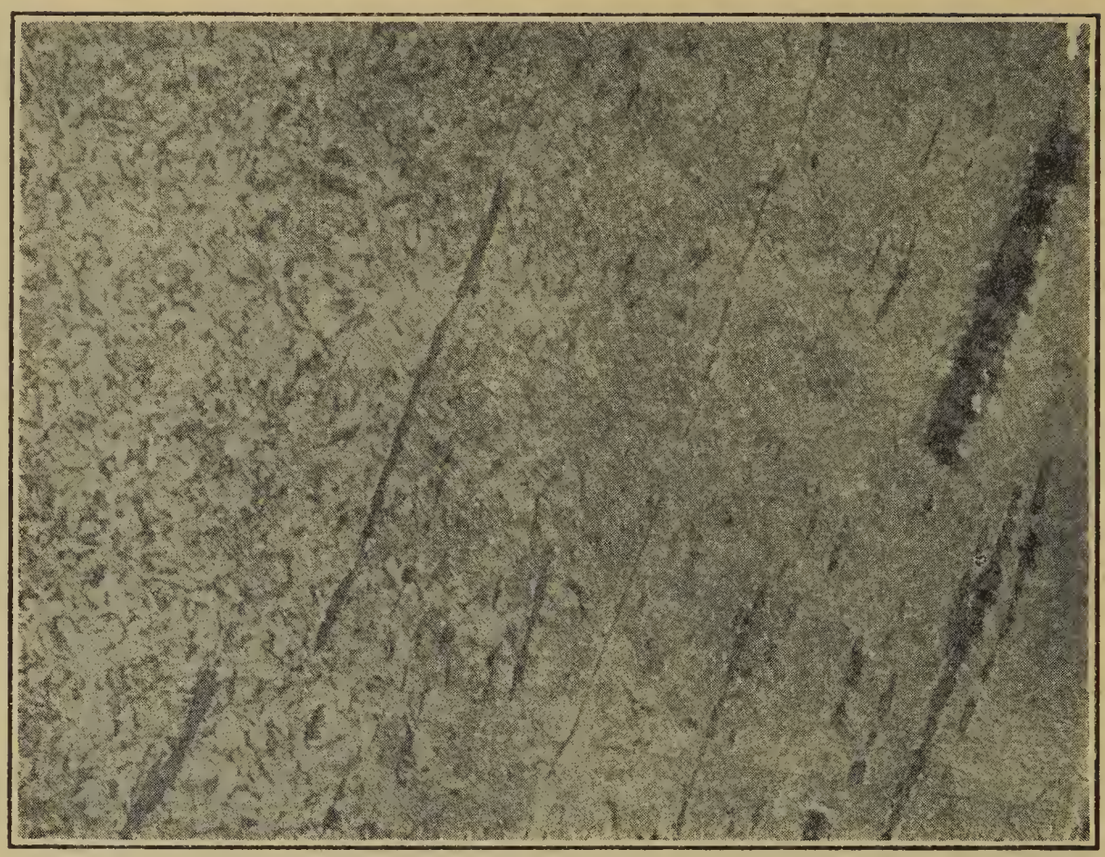


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FIG. 6. Swedish Iron. Junction of Medium and Low Carbon Areas with Slag Lines.

× 70

FIG. 7. High Purity Iron. Good, Clean Ferrite Structure.

influence upon the subsequent rate of rust formation; that the adherent rust, instead of acting as a protection, has a reverse influence.

The tests above recorded present data from which a quantitative idea of the influence of this factor may be derived. Samples marked (*a*) and (*d*) in Tables I and II, were exposed to two successive periods of rusting, the rust having been removed at the end of each period. At the same time similar test pieces (*b*) and (*c*) were exposed without disturbance for the entire 150-day period. If the presence of rust exerts an accelerating action, this will result in the total amount of corrosion from the 150-day samples being greater than for the sum of the corrosion of the two 75-day periods. This relationship is shown in Table V. The first and second columns give the corrosion factors for the two 75-day periods, the third column the average of these two periods. The fourth column gives the corrosion factors for the 150-day period. The ratios of the values of the fourth to the third column give the figures for the last column, which indicates whether there has been an accelerating or a retarding influence caused by the presence of rust.

From this table it is seen, that when subjected to atmospheric corrosion, there has been an accelerating action on all materials except cast iron; while with the materials exposed to fume corrosion the presence of the rust coating seems to have exerted a protective action on all but three of the materials. It is, of course, evident that these ratios would be different, depending upon the lengths of time of exposure. The accelerating action is probably greater when there is only a small amount of rust on the surface than when the rust increases in thickness.

The deduction of particular interest from this table is that the kinds of conditions by which rusting is produced are of importance, and that external conditions as well as internal structure and purity of material must be considered in studying iron corrosion.

Influence of Pitting.

It is obvious that the rate of deterioration of iron is measurable not only by the loss of weight, but that the depth of pitting is a factor which must be included. An attempt is made here to give

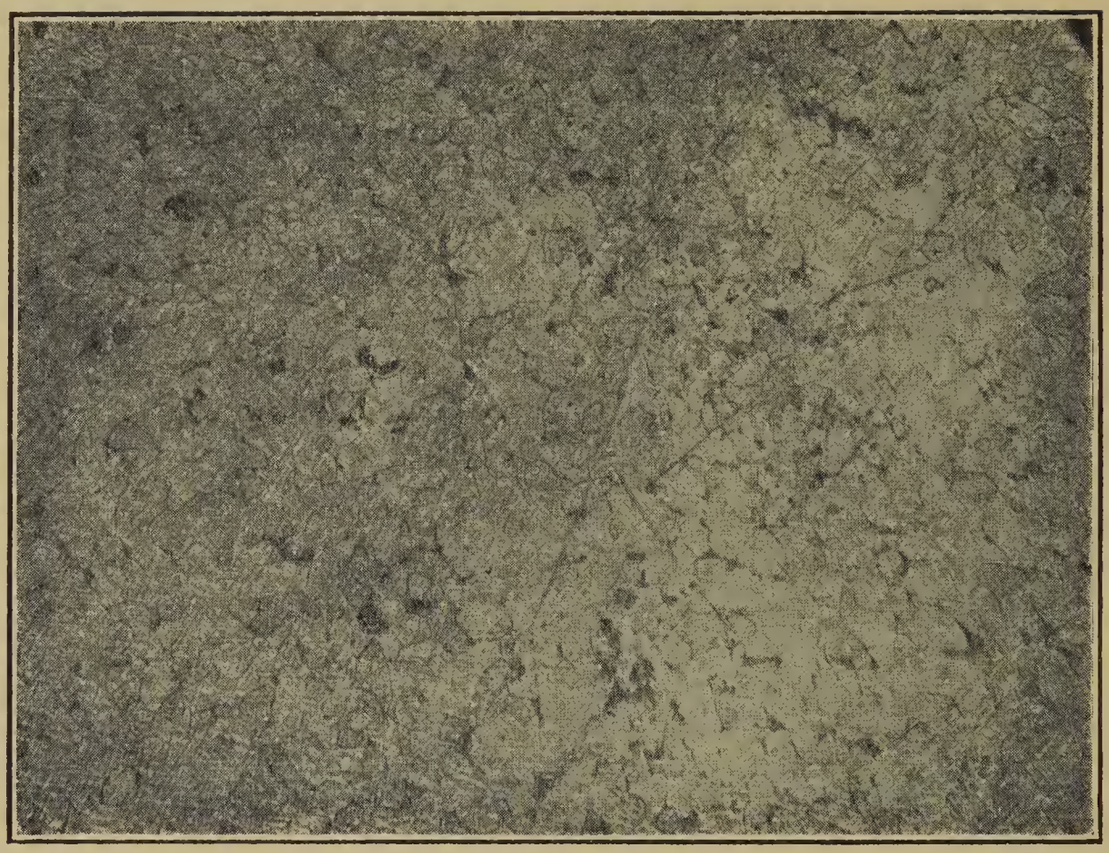

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FIG. 8. Open Hearth Plate.
Ferrite and Small Pearlitic Areas, Indicating Low Carbon Content; Few Inclusions, Indicating Good Material.

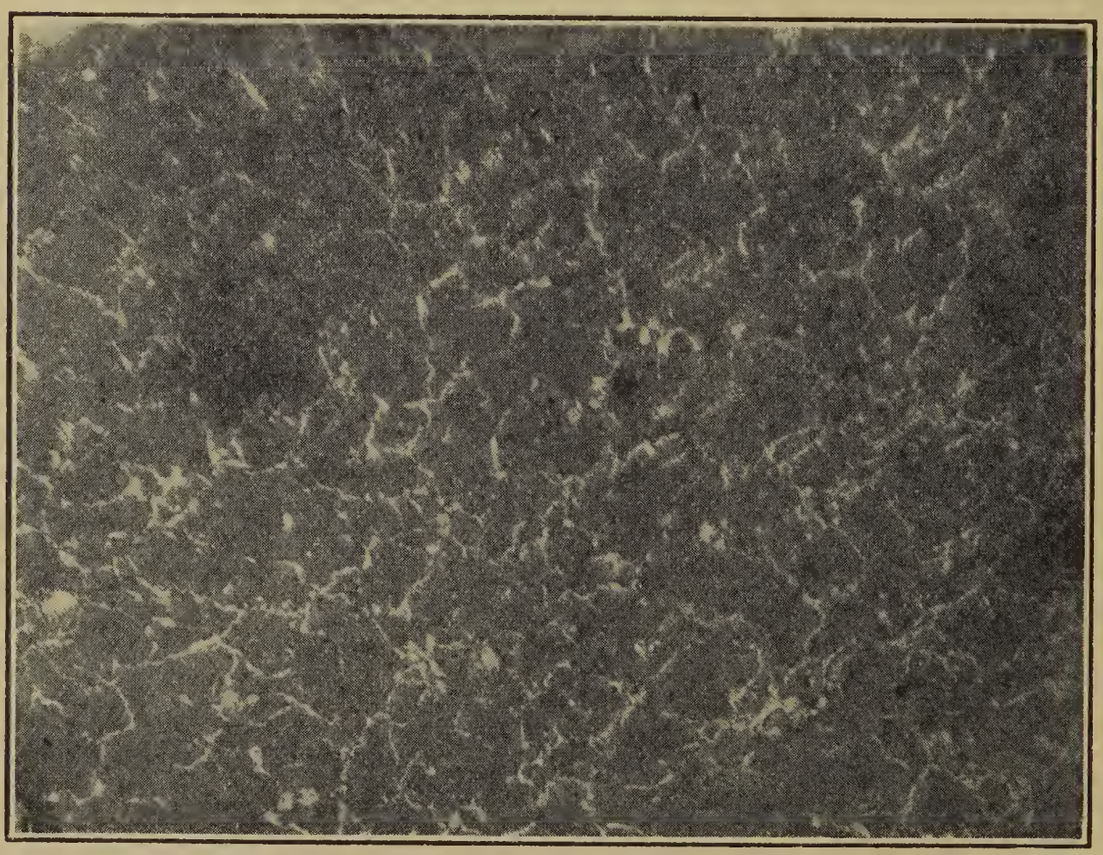

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FIG. 9. Bessemer Rail Steel.
Normal Structure of Rail from Reheated Billet and Rolled Hot.

a quantitative idea of this factor. It is unfortunate that all of the samples could not be tested for pitting effect. The thin sheet samples had been rendered too thin to be subjected to accurate grinding for removal of the pit marks and only the bar samples were examined.

TABLE V.

Accelerating Influences of Rust on Rusting.—Relative Corrosion Factors.

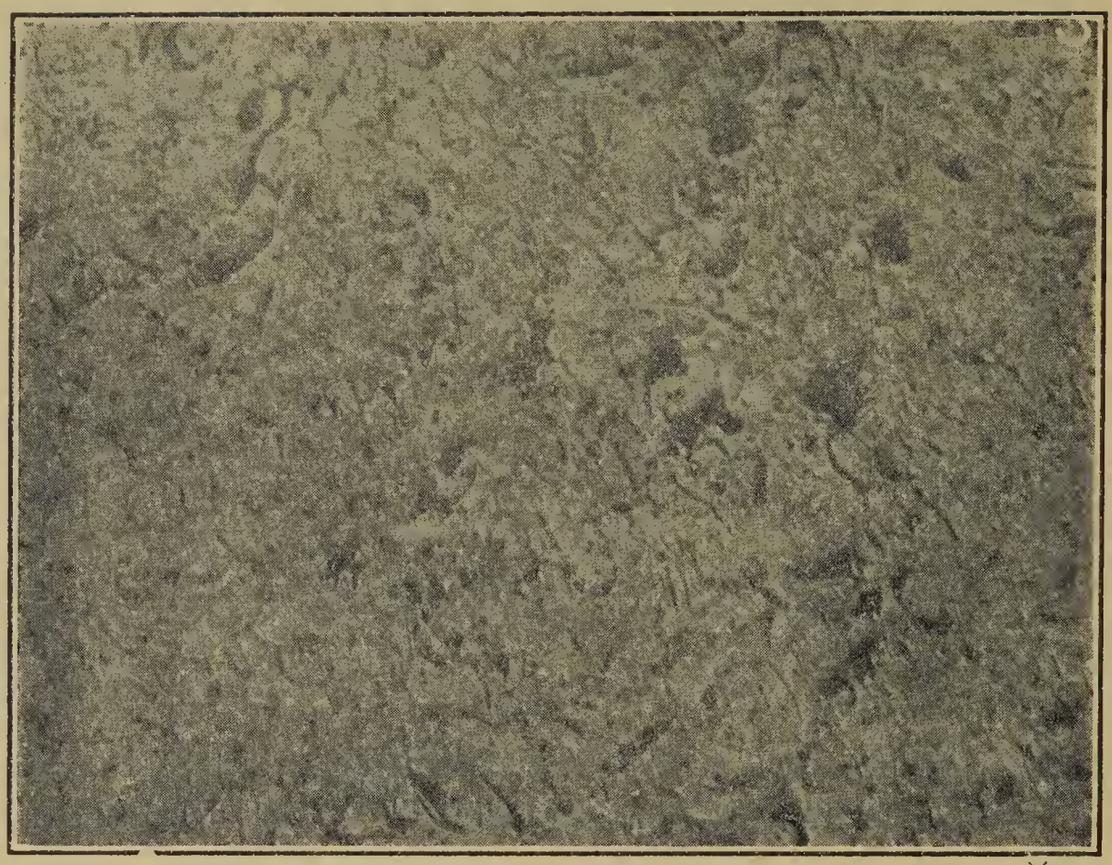
Atmospheric Corrosion.

Material	1st Period 75 days	2nd Period 75 days	Average	Combined Period 150 days	Accelerating factor (percent)
1	100	134	117	154	131
2	94.5	109	101.7	143	140
3	148	135	141.5	149	105
4	124	124	124	135	109
5	82.5	96	89.2	141	158
6	97	123	110	135	122
7	141	193	167	177	106
8	169	175	172	185	108
9	121	460	290.5	307	106
10	137	276	206.5	254	123
11	91	95	93	123	132
12	113	105	109	91.5	84

Fume Corrosion.

1	147	305	226	211	93
2	146	325	235.5	207	88
3	157	305	231	193	83
4	128	299	213.5	200	94
5	133	244	188.5	144	76
6	138	251	194.5	179	92
7	116	280	198	134	68
8	163	337	250	377	151
9	185	303	244	256	105
10	173	307	240	340	142
11	97	140	118.5	87	74
12	117	150	133.5	115	86

The materials, Nos. *1, 2, 5, 6, 11* and *12*, which had been rusting during the 139 and 300-day periods, were filed down and ground smooth until the pit marks had just disappeared and the amount of metal removed by this mechanical operation was determined. This was reduced to weight per square inch and



× 70

FIG. 10. Grey Cast Iron, Unetched, showing Graphite Distribution.

× 70

FIG. 11. Low Carbon Steel. Special Mechanical Treatment.

added to the corrosion loss per square inch. This combined value is taken as representing the combined deterioration by rusting and pitting, and the ratio of this amount to that due to rusting alone is indicated by what we choose to call the "Pitting Factor." The results are recorded in Table VI.

Table VI.

Influence of Pitting.

Atmospheric Corrosion.

Description of Material	139 Day Period			300 Day Period		
	Corrosion loss g. per sq. in.	Corrosion and Grinding loss g. per sq. in.	Pitting factor	Corrosion Loss g. per sq. in.	Corrosion and Grinding loss g. per sq. in.	Pitting factor
1. High purity iron ½ in. (1.25 cm.) thick.	0.1014	0.4874	4.8	0.2193	1.0433	4.76
	0.095	0.456	4.8			
2. High purity iron ¼ in. (0.65 cm.) thick.	0.0752	0.4072	5.41	0.230	0.885	3.86
	0.0853	0.4523	5.30			
5. Swedish wrought iron.	0.093	0.423	4.55	0.1995	0.9105	4.57
	0.0623	0.404	6.52			
6. O. H. steel boiler plate.	0.0658	0.3398	5.16	0.272	1.022	3.76
	0.0621	0.3061	4.93			
11. Bessemer rail steel.	0.0764	0.4344	5.68	0.1756	0.9566	5.45
	0.0668	0.3638	5.44			
12. Cast iron.	0.0763	0.4223	5.54	0.253	0.888	3.51
	0.0698	0.3838	5.50			

Fume Corrosion.

1. High purity iron ½ in. (1.25 cm.) thick.	0.168	0.609	3.63	0.5219	0.9739	1.86
	0.1601	0.555	3.47			
2. High purity iron ¼ in. (0.65 cm.) thick.	0.1382	0.4483	3.25	0.507	0.855	1.68
	0.1497	0.4387	2.94			
5. Swedish wrought iron.	0.121	0.3125	2.58	0.336	0.740	2.2
	0.113	0.417	3.69			
6. O. H. steel boiler plate.	0.1585	0.5615	3.54	0.3054	0.7504	2.46
	0.1375	0.5145	3.74			
11. Bessemer rail steel.	0.1053	0.4683	4.59	0.1756	0.555	3.18
	0.1196	0.4516	3.78			
12. Cast iron.	0.0925	0.3665	3.96	0.186	0.491	2.64
	0.1064	0.3704	3.48			

The fact of interest drawn from this table is that the combined effect of rusting and pitting under atmospheric conditions is from 3.5 to 6.5 times that as measured by the rusting alone, while under the fume corrosion conditions the pitting is much

less pronounced, as represented by the corresponding ratios between limits of 1.68 and 3.96. While the loss by rusting for the 300-day period is much the greater under the fume conditions, the pitting is less marked and the total deterioration is less.

Photographic records of the appearance of each of the samples after corrosion were obtained, a typical one being presented in Figures 2 and 3. This is for the open-hearth plate steel. There was a striking similarity of appearance as between the various materials and it is for this reason that only one is presented here. The fact that there has been less pitting under the fume than under atmospheric conditions is clearly shown.

Microscopic examination was also made of the various samples to determine if possible how the rate of corrosion may have been dependent upon internal structure. Some of these sections, magnified to 70 diameters, are presented in Figures 4 to 10.

It is a prevalent impression that corrosion, rusting and pitting are dependent upon the impurities in the metal, upon the internal structure, and especially upon segregation; that if there is absolute uniformity, absolute purity, and absence of slag, oxide and other inclusions, there will be minimum rusting. These impressions do not appear to be borne out by this investigation. The Swedish iron is shown in Figures 4, 5 and 6 to be markedly heterogeneous, there being some areas of pure ferrite, but others of medium carbon content and with slag inclusions. Fig. 7 shows good uniformity in one of the commercially pure irons, while other microphotographs not shown here indicate spots of impurity. In preparing these microphotographs it was the intent to make them representative of the average appearance of the samples rather than to emphasize impurities or non-uniformity.

SUMMARY.

1. The range of durability of various grades of commercial materials when exposed to a 300-day atmospheric test is represented by the ratio of about one to three. When exposed to the acid test the ratio is very much greater, being one to one hundred and sixteen.

2. The average rate of normal atmospheric corrosion under conditions found in Madison, Wis., is 5.777 g. per sq. dcm. per year. For a 16-gauge plate (0.16 cm. thick) exposed on both sides and assuming uniform corrosion this would mean a complete disappearance in about 11 years.

3. The corrosive action of the atmosphere may be influenced by fumes and smoke, so as to influence in marked degree the durability of iron, and that material most durable under one set of conditions may not necessarily be the most durable under others.

4. Since the service conditions constitute a vital factor in determining the rust-resisting power of iron, a study of these conditions is equally important with a study of the materials themselves.

5. The seasons and the weather conditions have a marked influence on the rate of corrosion.

6. The sulphuric acid test is not a satisfactory guide for estimating the rust-resisting power of a metal. It has a certain usefulness in investigative work, but is of little value as a practical test.

7. The ordinary black scale does not appear to be a retarder of atmospheric rust. Pitting causes deterioration in a year's time approximately three times as great as would rusting if distributed uniformly over the surface.

8. While impurities in the metal undoubtedly have an influence on the rate of rusting, it is evident that, although some are detrimental, others may be beneficial. Little accurate information appears available on this matter.

9. Heterogeneity of structure of metal is generally supposed to be antagonistic to durability, but this investigation shows that if it is a factor it is one of secondary significance and overshadowed by other factors.

These results are presented as tentative only, since conclusive evidence on a problem so important and complicated as the cor-

rosion of iron and steel can be obtained only by repeated tests upon a large number of samples.

The authors acknowledge their indebtedness to Mr. E. C. Haag in making many of the measurements recorded in this paper, and to the Northern Chemical Engineering Laboratories, in the preparation of specimens and co-operating otherwise in the work.

University of Wisconsin.

A Paper read at a Joint Session of Sections Xa: Electrochemistry, and Ve: Paints, of the VIII International Congress of Applied Chemistry, in New York City, September 11, 1912. Dr. W. H. Walker in the Chair.

INFLUENCE OF VARIOUS ELEMENTS ON THE CORRODIBILITY OF IRON.

By Charles F. Burgess and James Aston.

Incidentally to an extensive investigation on electrolytic iron and alloys produced therefrom, as carried out under a grant made a number of years ago by the Carnegie Institute, tests were made upon the corrodibility of a number of alloys. Acknowledgment is made to Mr. B. F. Bennett for his assistance on this particular phase of the work.

The electrolytic iron which has been used as a basis for the alloys, when compared with materials commercially available, may be taken as essentially pure, and in making up the alloys care was taken to exclude impurities as far as possible. The method of preparing the test samples consisted in first melting the electrolytic iron or the electrolytic iron alloy in closed graphite magnesia-lined crucibles heated in an electrical resistor furnace. Upon cooling down, the small ingots weighing from one to two pounds were forged into rods and strips. Only those alloys which would forge readily into shape were included in these tests.

From the forged bars samples were taken for chemical analysis, and through the courtesy of Messrs. Booth, Garrett and Blair, of Philadelphia, the determinations given in the first column of the attached table were obtained.

The corrosion test samples were about 2 x 1 x ⅛ in. (5 cm. x 2.5 cm. x 3.1 mm.). They were exposed to the weather conditions in Madison, Wis., for a period of 162 days, from July, 1909, to February, 1910. Before exposure all samples were ground to a uniformly smooth surface. After the removal of rust by the ammonium citrate method, all samples were subjected to an accelerating acid-corrosion test, using a twenty percent sulphuric acid and immersing for a period of one hour. Each

sample was suspended by itself in a beaker, to avoid errors by presence of other materials.

Some results of interest were derived from these tests, though how far they may be of practical value as indicating the influence of various elements on commercial material is problematical. The materials used are practically carbon free, and with such minor quantities of sulphur, phosphorus, silicon and manganese (except where intentionally added) as would have, in all probability, little effect. There is a widely prevailing belief that the effect of any element added to iron is to increase corrodibility, by furnishing galvanic couples. A great majority of these test samples indicate the reverse; that is, a greater durability for the alloys than for the electrolytic iron base.

Comparisons between the corrodibility of electrolytic iron and certain forms of pure commercial iron on the market indicate that electrolytic iron is more corrodible both in the atmosphere and in acids. In fact, no quantitative comparisons have been attempted between the alloys produced in this investigation and commercial materials. As an approximate indication, however, ranges are given for tests on commercial materials at the bottom of the table for the experimental alloys.

Electrolytic Iron.

The electrolytic iron for which data are given in the table is not introduced as a sample of the purest that can be made, but is rather average material, serving as a good representative standard for comparison. As a matter of fact, during the course of the tests, as will be noted at the foot of the table of data, figures were obtained upon various grades of iron and steel of commercial grade and of widely varying degrees of purity; and in these results may be noted values of corrosion both higher and lower than those of the electrolytic-iron sample.

So far as this particular sample is concerned, it shows nothing especially striking in resistance to corrosion either in acid or in the atmosphere.

In the acid test, in particular, it does not fall in line with the commonly accepted view that a close approach to purity would indicate a high resistance to acid attack. On the contrary, this particular material has been attacked even more severely than most of the alloy samples tested at the same time.

Aluminum.

In this series there are not enough data to warrant definitive deductions. So far as the sample with 0.067 percent of aluminum is concerned, this may be taken as corresponding to iron free from alloying agents. The second sample, carrying 1.33 percent of aluminum, shows an even higher attack by acid than the one of the lower aluminum, but there has been a slight falling off in the atmospheric corrosion. However, there has been nothing striking in either case.

Arsenic.

In view of the fact that the presence of small amounts of arsenic in sulphuric acid pickling solutions decreases markedly the rate of the attack, it has been suggested frequently that arsenic present as an alloying constituent of steels might make such steel more resistant to corrosion, particularly to acid corrosion. This, however, appears to be an erroneous assumption, as increased corrosion in acid has been shown by Heyn and Bauer, and by Berthier. No satisfactory or conclusive work seems to have been done on the resistance of these materials to atmospheric influences.

Our results cover a series in which arsenic ranges from 0.29 percent to 3.56 percent, and we find a fair resistance to the acid attack, which resistance falls off appreciably with increase of arsenic content. On the other hand, the corrosion in the atmosphere is somewhat on a par with that of the electrolytic sample, and there would seem to be no particular merit in the use of arsenic alloys for resisting atmospheric corrosion.

From the point of view of physical qualities also, this series would not be of particular value, since the brittleness and weakness resulting from the addition of arsenic would be serious. Addition of arsenic seems to result in high magnetic qualities, but it is an element which is difficult to add, and if of service from the corrosion point of view it would have to be added in very large amounts, resulting in a structurally or mechanically poor material.

Cobalt.

In view of the close relationship in the general properties of cobalt and nickel, it might be natural to expect that the use of

these elements as alloying agents would result in somewhat similar properties. The series here tested, however, in which the cobalt varies from 1.3 to 5.5 percent does not point to any close relationship. The resistance to acid of this series is not particularly striking, but does fall off appreciably with increasing cobalt content. The same general effect is noted in the atmospheric tests; but while the corrosion is fairly low, there is not the same resistance to atmospheric attack as is obtained by the addition of the same quantity of nickel. This series shows a fairly close relationship in the rates of atmospheric and acid attack.

To use cobalt for the purpose of making a material highly resistant to corrosion would seem to demand considerable quantities of this element. There would be no advantage, therefore, in the use of this metal as compared with nickel, in view of the high relative cost of the cobalt.

Copper.

The influence of copper upon the corrosion of iron and steel, and to some extent, as well, upon the other physical properties is, at the present time, a matter of controversy. So far as the resistance to acid attack is concerned, particularly to sulphuric acid, the evidence seems to be convincing that copper additions result in marked decrease in the rate of such attack. There is a tendency also, not supported by conclusive tests, to believe that copper additions will likewise increase the resistance to atmospheric corrosion.

The series herein tabulated, in which the copper ranges from 0.089 percent to 7.05 percent have the expected high resistance to acid attack and also show a low corrosion in the atmosphere. The latter is of particular interest, inasmuch as the values are consistently low throughout the series, and the markedly beneficial results seem to be obtained from even small amounts of added copper.

In view of the materially improved physical properties resulting from one to two percent of copper additions, together with the low cost of such addition and the corrosion resistance herein noted, it would seem that this series is of particular promise and worthy of extended study. The quality, both mechanically

and from the corrosion point of view, is entirely comparable with that resulting from the use of corresponding amounts of nickel and, of course, there is a materially lessened cost for the addition.

The exact reason for the decreased corrosion is somewhat a matter of speculation. Considering that iron and copper form solid solutions, at least up to three percent or thereabouts of copper addition, or well within the limits of commercial utility, we should expect the structure of the resultant alloy to be one of perfect homogeneity. There should, therefore, be no internal influence tending to promote increased electrolytic action, and the effect of the dissolved copper should at the very worst be merely neutral as far as corrosion is concerned. In fact, increased resistance to corrosion might be expected, since the solid solution of the two elements might decrease the solution tendency of the iron; or if the iron finally goes into solution, it may leave a deposit of copper, forming a film and protecting the underlying metal from further attack. The presence of such a copper film has been observed repeatedly in the course of etching of samples for microscopic examination and has been noted by other investigators during acid attack of copper-iron alloys. This speculation seems to be confirmed by the tests herein enumerated.

Lead.

But one alloy of this series was tested, and that contained only 0.061 percent of this element. The acid corrosion is the same as that observed by the electrolytic iron, while the atmospheric corrosion has dropped to about half the figure of electrolytic iron. Not enough data are at hand, however, to warrant any deductions regarding the influence of lead upon the corrosion of iron.

Manganese.

The supposedly increased corrosion of modern steels as compared with the older iron has generally been ascribed to the presence of manganese, which is present in the later-day materials as a result of modern processes of manufacture. It may be, however, that the manganese is blamed for results due to the other elements associated with it, or perhaps to other factors resulting from modern conditions of manufacture.

So far as our tests show, in this series, which runs from 0.50 percent manganese to 10.42 percent manganese, there is nothing worthy of particular comment either in the acid or atmospheric corrosion. There is considerable inconsistency in the results, and the atmospheric tests in particular seem to indicate a slight increase of corrosion with increase of manganese content, though in all cases the corrosion was less than for the electrolytic iron alone.

The alloying relations in this series are those of solid solution, in this respect similar to the copper-iron alloys in the useful range. We have, therefore, a homogeneous structure and no internal causes for electrolytic action. However, in view of the very similar properties of the two metals, there would probably result but little change in the solution tendency of the alloy as compared with the iron itself. Also there would be no deposition of a protective film, as was mentioned in the copper series, since manganese is attacked very much like iron and would rust away in a similar manner. Consequently rust once formed from solution of either metal should aid rather than retard further progress of the corrosion.

Nickel.

This series shows alloys notably good both in the acid and atmospheric tests. There is a general tendency for increased resistance with increased nickel content.

Within the nickel content used in practice, about three percent, we note a marked falling off in atmospheric corrosion. The hindrance to the general use of this property is the relatively high cost of the nickel addition, and it would seem that these alloys would not be of particular merit unless the use of the material is also warranted by the increased strength resulting from the addition. The highest resistance noted lies well up in the series, at ten percent nickel and above. Such alloys would be beyond the range of general commercial utility, not only because of the high cost of the nickel, but because of the hardness and brittleness and generally disadvantageous physical properties in this region of the series.

The alloying relations of nickel and iron are those of solid solution, and it would seem that the protective effect is due perhaps to the same reasons cited in the case of the copper-iron

alloys; that is, we would have very probably a markedly decreased solution tendency, and in case of any corrosion it would result in a solution of the iron and the consequent concentration of the nickel as a surface-protecting film.

Selenium.

There was tested but one alloy of this series, with the very low content of 0.017 percent of selenium, consequently no particular deductions can be drawn. The acid resistance in this particular sample is very low, while the corrosion in the atmosphere is noticeably high.

Silicon.

In this series the silicon content varied from 0.23 percent to 2.82 percent. The corrosion values are in general high and somewhat conflicting. In fact, this series seems to have suffered the greatest corrosion noted. There is a general tendency for increase in the atmospheric corrosion with increase of silicon content, but not a very material increase.

There seems to be an inclination to assume increased resistance to corrosion in the silicon steels, but the only reliable data appear to be those obtained upon acid tests, and mainly upon acid tests of the alloys of high silicon content. Here a compound of iron and silicon becomes the principal constituent, and the resistance to acid is probably due largely to this.

So far as ordinary amounts of silicon are concerned, its use seems to be disadvantageous both in acid and atmospheric corrosion. Also, silicon behaves much like arsenic and, while it results in good magnetic qualities, the resultant steels are otherwise poor physically, being brittle, weak and hard to work.

Silver.

Although alloys were made in which the added amount of silver was as high as ten percent, the resulting alloys actually indicated a maximum of 0.69 per cent retained, and the series here cited has a silver content varying from 0.28 percent to 0.69 percent. There is no particular merit in this addition so far as either acid or atmospheric corrosion is concerned, and all of the figures are closely comparable to that obtained with electrolytic iron alone. There is, of course, no particular commercial

significance attached to the use of iron-silver alloys, because of the relatively high cost of the addition.

Tin.

This series has a tin content varying from 0.28 to 1.56 per-cent. In the lower end of the series the resistance to acid attack is particularly good, but the corrosion in acid increases perceptibly with the higher content of tin. As far as the atmospheric tests are concerned there is nothing of particular moment. There is a slight falling off however with increase of tin. The iron-tin alloys are somewhat similar in their general properties to the iron-arsenic and iron-silicon alloys,—that is, all of these additions result in improved magnetic quality of material, but at the expense of the physical, and the resulting alloys are brittle and weak and hard to work.

Tungsten.

The tungsten varied from 0.40 percent to 23.86 percent. In the acid test the results are all good, some of them very strikingly so; but there is a general irregularity in the figures. The same is true in regard to the atmospheric tests, with a seeming tendency toward decreased corrosion with increased tungsten content.

However, the general results are not especially worthy of attention, and considering the fact that any markedly decreased corrosion is obtained only after high tungsten additions, these alloys do not offer special value from the corrosion standpoint, since with the high tungsten additions we are entering the tool-steel range of alloys of high cost and extreme hardness and brittleness.

Conclusions.

These tests, covering several series of alloys of iron with other elements, do not seem to point to any quantitative relations between the acid and atmospheric corrosion.

So far as the atmospheric tests are concerned, numerous alloys can be noted in which the corrosion is less than in the electrolytic iron. The copper series would seem to offer particular advantages in view of the beneficial results obtained with small copper additions and because of the consistently low values throughout the series. Again these benefits are obtainable without prohibitive cost for the addition agent.

		Acid Corrosion	Atmospheric Corrosion	
		g. per sq. dcm.	lb. per sq. ft. per year	Kg. per sq. meter per year
Electrolytic Iron		1.30	0.1025	0.499
	Percent			
Aluminum—	0.067	0.628	0.110	0.513
	1.333	0.760	0.080	0.39
Arsenic—	0.292	0.448	0.083	0.405
	0.430	0.815	0.0703	0.343
	0.951	0.405	0.0870	0.425
	1.810	0.131	0.072	0.352
	3.862	0.086	0.064	0.312
	4.141	0.102	0.074	0.361
	3.562	0.144	0.063	0.306
Cobalt—	1.035	0.705	0.049	0.239
	2.000	1.02	0.070	0.342
	4.055	0.356	0.042	0.205
	5.052	0.257	0.042	0.205
Copper—	0.089	0.178	0.052	0.254
	0.202	0.095	0.039	0.190
	0.422	0.059	0.055	0.268
	0.592	0.112	0.050	0.234
	0.804	0.104	0.053	0.259
	1.006	0.067	0.046	0.225
	1.51	0.147	0.046	0.225
	2.005	0.091	0.051	0.249
	3.99	0.093	0.035	0.171
	5.07	0.087	0.031	0.151
	6.16	0.143	0.041	0.200
	7.05	0.186	0.033	0.161
Lead—	0.061	1.30	0.056	0.273
Manganese—	0.505	0.56	0.055	0.268
	1.00	0.52	0.080	0.390
	2.00	0.725	0.062	0.302
	3.00	1.11	0.067	0.327
	10.419	0.352	0.089	0.435
Nickel—	0.27	0.633	0.059	0.288
	0.56	0.547	0.071	0.347
	1.07	0.507	0.058	0.283
	1.93	0.192	0.023	0.112
	7.05	0.226	0.038	0.185
	8.17	0.125	0.029	0.141
	10.20	0.091	0.027	0.132
	11.29	0.123	0.027	0.132
	12.07	0.084	0.024	0.117
	13.01	0.237	0.031	0.151
	19.21	0.072	0.018	0.088
	22.11	0.0254	0.020	0.098
	25.20	0.054	0.023	0.112

		Acid Corrosion	Atmospheric Corrosion	
		g. per sq. dcm.	lb. per sq. ft. per year	Kg. per sq. meter per year
	Percent			
Nickel—	26.40	0.554	0.021	0.102
	28.42	0.155	0.021	0.102
	35.09	0.183	0.018	0.088
	47.08	0.160	0.0126	0.062
	75.06	0.049	0.0044	0.0215
Selenium—	0.017	0.190	0.1385	0.676
Silicon—	0.233	1.63	0.104	0.509
	0.603	1.19	0.076	0.370
	1.033	0.85	0.106	0.518
	1.897	0.80	0.124	0.606
	2.826	1.27	0.130	0.635
Silver—	0.281	1.02	0.065	0.317
	0.492	1.76	0.090	0.430
	0.581	1.34	0.073	0.356
	0.691	1.17	0.092	0.450
Tin—	0.288	0.284	0.069	0.337
	0.342	0.350	0.039	0.190
	0.686	0.386	0.049	0.239
	1.568	1.03	0.058	0.283
Tungsten—	0.406	0.363	0.076	0.371
	0.925	0.088	0.062	0.302
	2.334	0.086	0.062	0.302
	3.553	0.332	0.063	0.308
	5.982	0.304	0.060	0.293
	9.849	0.398	0.040	0.195
	13.641	0.365	0.049	0.239
	23.866	0.183	0.044	0.215

Various grades of low carbon iron and steel.....0.300 to 0.73
High carbon steel 0.278
Cast iron—scale removed 0.770

Chemical Engineering Department,
University of Wisconsin.

DISCUSSION.

DR. A. S. CUSHMAN: Laboratory studies such as are described in these papers are very valuable, and bring out points that are well worthy of our attention and discussion, and that, perhaps, have not been carefully enough considered heretofore. With respect to the first paper, I wish to state that it is unquestionably true that in the alloy field we have the opportunity of stumbling on combinations of metals which may prove far more resistant to corrosion than the purest iron that can be made. Whether or not such alloys can be manufactured for a cost which will be practical and attractive remains to be seen. Electrolytic iron is interesting to test because of its freedom from metallic impurities. It is, however, saturated with hydrogen, and to that extent is itself an alloy. In this respect it probably differs from iron which has been annealed in hydrogen, where the hydrogen is probably held in some form of solution or inclusion. If the electrolytic iron is melted it is probable that most of the hydrogen is driven out, but it is by no means certain that it is entirely eliminated by this treatment. This point should not be lost sight of in considering electrolytic iron as a material of standard purity.

My experience has led me to doubt the value of laboratory corrosion tests, or even atmospheric corrosion tests that depend upon cleaning off the rust and re-weighing the specimen. The fact that it has been shown pretty conclusively that all corrosion phenomena are connected with electrolytic effects which take place on the surface of the corroding metal, and since a piece of metal which is rusting is not losing weight at the electro-negative areas on the surface, it is quite possible that of two samples, the one which is losing the least weight is really suffering the most under the conditions of the test. In fact, in my experience, which now extends over quite a number of years, in observing corrosion phenomena and testing various samples I have frequently made this observation, namely, that the specimen which was rusting more evenly and losing weight very slightly from all over its surface would show up the worst on the weight records, whereas the other piece which is rusting and pit-holing through does not lose so much weight. So far nearly all acceleration corrosion tests made by different observers have depended upon making a

record of loss of weight of the specimens, and I wish to point out the danger of error and being drawn to wrong conclusions by such methods of testing. To make myself still clearer, let us suppose that we are dealing with two pieces of sheet metal of exactly the same size and thickness. Now, suppose we wish to remove from these two specimens samples for analysis and at the same time destroy the specimens as little as possible by the removal of the sample. If one of the specimens was attacked with a planer, a very slight shaving might be taken off the entire surface without damaging the test piece to any considerable degree, whereas if the other specimen was attacked with a drill it would be impossible to take an equal weight off of it without actually destroying the integrity of the specimen by drilling holes through it or almost through it. With these considerations in my mind, I wish very emphatically to state that conclusions drawn from weight loss under corrosion tests are dangerously misleading, and in some cases would cause us to form an opinion diametrically opposite to the truth. I quite agree with the authors in regard to the unsatisfactory nature of the acid test, but, unfortunately, all other acceleration tests so far proposed are equally unsatisfactory. I do believe that the acid test gives some valuable information in regard to a material, if it is properly interpreted and applied. As far as exposure tests of bare specimens to atmospheric conditions are concerned, I agree with Prof. Burgess that results may vary in different parts of the world, owing to climatic conditions and depending upon the prevailing winds which blow with reference to the surface of the test piece, and upon the character of the prevailing atmosphere with regard to acid impurities. It should also be pointed out that neither iron nor steel is manufactured to be exposed to the weather without any form of protective coating. With the exception of the insides of boilers, tanks and pipes, and possibly also heavy chains, iron is not directly exposed to the corroding medium without some form of protective coating, and the condition of exposure of iron and steel in this sort of service is nothing like the attack made upon the metal by exposure, for instance, on the roof of a building. After all, the long time experience of consumers with reference to any given type of ferrous metal must continue to be of more value in forming a judgment than the

results of any accelerated tests, whether in the laboratory or on exposure of bare plates or sheets to the outdoor atmosphere.

Dr. W. H. Walker: I am very much interested to learn that Prof. Burgess has found that manganese is not deleterious in iron, inasmuch as I have held this opinion from the first. In fact, manganese should decrease the corrosion of a sample of iron rather than increase it. The fact that samples of steel which corrode rapidly are frequently found to be high in manganese has been made the basis for the opinion that manganese is itself harmful. I believe that it is manganese oxide that does the harm, but not metallic manganese. A fact which may be easily observed in Boston, where the switches and frogs of the trolley system are made from manganese steel, is that after a rain the ordinary steel rails will rust rapidly, while the frogs remain perfectly bright.

Mr. Bradley Dewey: In connection with Dr. Cushman's criticisms of the manner in which Professor Burgess carried out his tests, I might state a few results which I have recently had the privilege of going over in some detail, although the work is not mine and is being done by Mr. D. M. Buck, who will probably describe it to the Society at some future date.

Mr. Buck has, at several places throughout the country, put up test roofs, made up of some half dozen or so full-sized sheets of each of many different grades of steels and similar products. At these same points there are small, I think 2 by 4 inches, test pieces in insulated racks. These test pieces are from the identical steels used to make up the full-sized sheet. Now, at the end of some months there are very marked differences in the condition of the various steels, those high in copper being in very good shape, while those Bessemer steels which are without copper have entirely broken down.

Recently, with the roof in this condition, and after a close examination and marking by several persons, who all checked reasonably well, the small test pieces were taken down and their loss in weight determined. In the light of Dr. Cushman's doubting that the small scale tests are ever in agreement with those carried out on a large scale, it is interesting to note that this loss in weight varied over very wide limits, and that in every case the degree of corrosion as determined in this method gave the

same order of value as did the grading of the actual large scale tests by the various observers.

Mr. R. H. Gaines: Prof. Burgess remarked in the course of his abstract that he had arrived at a conclusion that certain foreign elements in iron and steel were not hurtful to the metal, whereas others were certainly corrosive by their presence. I would like him to state what elements he considers as deleterious and what non-deleterious.

Dr. W. H. Walker: I would like to ask a question on the same line. I was interested to hear him state that he did not regard heterogeneity in the sample as controlling, but as rather of secondary importance. I understood from someone that Dr. Heyn, of Berlin, had given the same opinion. I would like to ask Prof. Burgess if he ever heard Heyn say that, or let us know what he said.

Prof. C. F. Burgess: The suggestion made by Dr. Cushman, that electrolytic iron may not be comparable to other forms of iron due to hydrogen content, cannot be denied. Since the material to be melted must pass the high temperature of 1,600° C., the amount of hydrogen which remains after this treatment must be exceedingly small and, therefore, the influence of this small amount should be comparatively slight. The properties of melted electrolytic iron are probably influenced more by oxygen than by hydrogen.

On account of the high purity, as determined by chemical analysis, and, on account of the reproducible uniformity of the material, it should constitute a desirable starting point for investigating the influence of the various elements when alloyed with iron, and on this assumption the numerous alloys referred to in the paper have been prepared. The alloys were made primarily for physical and electrical tests, and it was an afterthought to subject them to corrosion tests. As a result there are not a sufficient number of samples containing some of the elements, such as sulphur and phosphorus, to determine the exact influence of such elements on corrosion. The point which appears of interest and suggestive is that the great proportion of elements seem to make electrolytic iron more resistant to corrosion, the notable exceptions being silicon and selenium. It must, of course,

be admitted that the influence of these various elements on electrolytic iron may not be exactly comparable to their influence on other forms of commercial iron and steel.

DR. W. H. WALKER: Is anyone present who happened to hear what Dr. Heyn said? I always felt that heterogeneity in iron was deleterious, although I must say I always in my own mind limited it to oxide.

MR. F. N. SPELLER: I referred to Prof. Heyn's remarks in discussion earlier in the afternoon. As I remember what he said last week on this matter, it was simply that as a result of his investigations he had come to the conclusion that the influence of purity had been greatly exaggerated and that ordinary rust once formed on the surface of the iron was a greater accelerator of corrosion than any of the foreign elements commonly found in iron or steel.

MR. W. D. RICHARDSON: Several years ago I read a paper before the Chicago Section of the American Chemical Society, and later on a similar paper before the Minneapolis meeting of the American Chemical Society, concerning certain experiments which I had carried on in regard to the corrosion of iron. The gist of the ideas presented was that the surface conditions, and especially rust, overbalance all the influences within the metal itself in determining the course of ordinary corrosion after corrosion is once started. The composition of the metal influences the commencement of corrosion, but after an adherent layer of rust is formed the rust is the predominating influence, so that nearly pure iron, iron containing a small percentage of copper, mild steel, etc.; in other words, metals of different composition will, if adherent rust is present, follow nearly the same line of corrosion. Of course, to produce the adherent rust, it is necessary to have oxygen present, also to have alternate wet and dry conditions, and these are the conditions prevailing in ordinary atmospheric corrosion. The experiments which I carried out bore out these ideas in general. I also advanced the hypothesis, as a part of the general proposition, that it is only when we have a clean surface and continuously maintain a clean surface of the metal, that the composition of the metal itself becomes of predominating importance in influencing the corrosion. We have these condi-

tions when carrying out corrosion tests in acids, and one of the great problems in corrosion was the difference in behavior between iron and steel of different composition, in dilute sulphuric acid, for example, and in the air. According to the hypothesis advanced, the differences noted in the early experiments between corrosion tests in acid on the one hand, and service tests, or tests simulating corrosion in service on the other, were due to the fact that in one case a clean surface was present, and in the other case there was an adherent coating of rust covering a part of the surface. Of course, if the rust covering were uniformly adherent all over the surface there would be no corrosion. There may be other surface factors also, but rust appears to be the most important. The hypothesis, as stated, may require considerable modification in respect to different details; probably it does. But it seemed to me then, and I have seen no evidence since to change my view, that it is true in its main aspect.

Dr. W. H. Walker: I think it is unquestionably true that there is one factor which we have not taken sufficiently into consideration in our study of the corrosion of iron, namely, the ability of a given sample to form a closely adherent protective surface of iron rust. The old bridge at Newburyport has stood for almost one hundred years, and the iron is still in a fine state of preservation, although the bridge itself has been replaced by a larger one. A piece of this iron when freed from its natural coating of rust is very heterogeneous and will corrode as rapidly in water as any sample of iron or steel I have ever seen, and yet, apparently, it is able to protect itself.

Mr. Edw. Weston: It has been the experience of the speaker with regard to water works service pipes that the character of the water has a very marked effect upon the rate of corrosion. While it is ordinarily true that after rusting is once started, due to imperfect coating of the pipe or imperfections in the coating of the pipe, it will go along very rapidly provided there is no deposit from the water on the inside of the pipe, yet if the condition occurs where the organic matter in the water causes the rust to take the form of an impenetrable film or lining, corrosion comes practically to a standstill after a few weeks or months. This has been noted repeatedly.

It is a well-known fact that very pure waters containing large amounts of carbonic acid and oxygen attack service pipes much more rapidly than surface waters containing organic matter in colloidal suspension. This matter will precipitate with the rust and form a film on the inside of the pipe. For this reason most surface waters can be used with lead pipe with impunity.

Most water works engineers are prejudiced in favor of the so-called old-fashioned wrought iron. There seems to be no scientific reason for this prejudice, but they speak in almost endearing terms of the pipe that they used to get. The speaker's own experience is that wrought iron pipe can be good and bad, and the same is true of steel pipe. It is difficult to tell by any ordinary test which pipe is iron and which is steel. If a ready test could be placed in the hands of the ordinary practicing engineer, it would be a great boon. It might help to determine which metals will resist ordinary corrosion and which will not.

In this connection some experiments by the writer with tin-lined lead pipe are of interest. Contrary to expectations, the tin lining did not protect the lead against solution; it only retarded it. No tin was dissolved from the pipe, but appreciable quantities of lead. The explanation of this lies in the well-known fact that tin crystallizes before it fully contracts, thus leaving interstices through which the water reaches the lead, and, furthermore, reaches it under electrolytic conditions very favorable to corrosion.

PROF. BURGESS: While taking part in an investigation of a stand-pipe failure last winter, a study was made of the quality of steel which entered into its construction. Certain portions of this steel were found to be badly pitted. In selecting one of the deepest pits and cutting a section it was found that the pit had a flat bottom, apparently formed by the presence of a layer of slag, or, perhaps more properly speaking, by so-called metallographic "ghost bands." The optical evidence pointed, in this case, to a retarding influence of impurity. This does not constitute absolute proof, but is suggestive that impurities producing heterogeneous material may have some merit.

Based upon extensive study and the occasional turning up of iron samples which seem to show remarkable durability, the writer believes that there is some important factor governing the

rate of corrosion which is not thoroughly understood; also, that there is consequently a possibility of discovering some new line of attack on this problem of making durable iron, which will be of importance. Certain laboratory investigations which will be reported upon later seem to point in this direction.

In attempting to prevent deterioration by rust there should be recognized a difference between the problem of preventing the initial rusting and the problem of preventing the pitting action to which Dr. Cushman has just called attention. Pitting is dependent upon an acceleration action produced by rust accumulation, and if a barrier can be interposed so that a rust spot will spread out rather than become deeper, there will be a minimizing of the damaging action. The writer believes that slag and other non-conductive impurities frequently found in iron, under certain conditions, constitute such barrier. A study of the influence of impurities must recognize, not only those which are alloyed with the iron and the metallographic relationship of the same, but those impurities which exist as included non-metallic compounds.

MR. GAINES: Do you mean to suggest that a half percent of silicon in wrought iron would render it more durable?

PROF. BURGESS: In all probability silicon as an alloy with the iron has a decidedly different influence on the corrosion than has silicon in the form of included slag. Silicon in the former condition appears to be disadvantageous, while in the latter there may be some advantage.

A Paper read at a Joint Session of Sections Xa: Electrochemistry, and Ve: Paints, of the VIII International Congress of Applied Chemistry, in New York City, September 11, 1912. Dr. W. H. Walker in the Chair.

A METHOD FOR TESTING THE MUTUAL CORROSIVE EFFECT OF METALS.

By Hugo H. Hanson and Warren K. Lewis.

It is being widely recognized that the acid test, as a measure of the resistance of iron and steel to corrosion under normal conditions, is unreliable and deceptive. Whipple & Whipple emphasize this in their paper. A trustworthy method of determining this resistance is highly desirable. A test for determining the relative values of paint films as protective coatings for iron and steel, devised by one of the authors (Walker and Lewis, Jour. Ind. Eng. Chem., **1**, 11 (1909)), developed by the late Mr. M. T. Jones, and used recently by Mr. W. C. Slade (*Ibid.*, **4**, 189 (1912)), is applicable to the study of the influence of one metal on the corrosion of another with which it is in contact, allowing the use of neutral solutions, if necessary of pure water, or of a particular water whose action it is desired to predict. The method consists in connecting electrodes of the two metals through an ammeter, keeping the solution about the electronegative metal saturated with air, and measuring the current in the external circuit.

The value of the electrolytic theory for correlating and utilizing the facts and phenomena of corrosion is underestimated by many, through lack of appreciation of the number and importance of the factors involved. At least three of these factors play controlling parts in all processes of atmospheric corrosion:

1. The electrolytic potential determines the direction of the reaction, though seldom the rate of corrosion. Thus pure zinc is strongly electropositive, and yet its rate of solution, even in relatively strong acids is very low, owing to the polarization encountered.

2. The ease of deposition of hydrogen upon the metal determines whether and how fast a metal electropositive to hydrogen will corrode in water in the absence of air, and probably plays

a large part in atmospheric corrosion, although it has hitherto been impossible to separate this effect from the phenomena of depolarization.

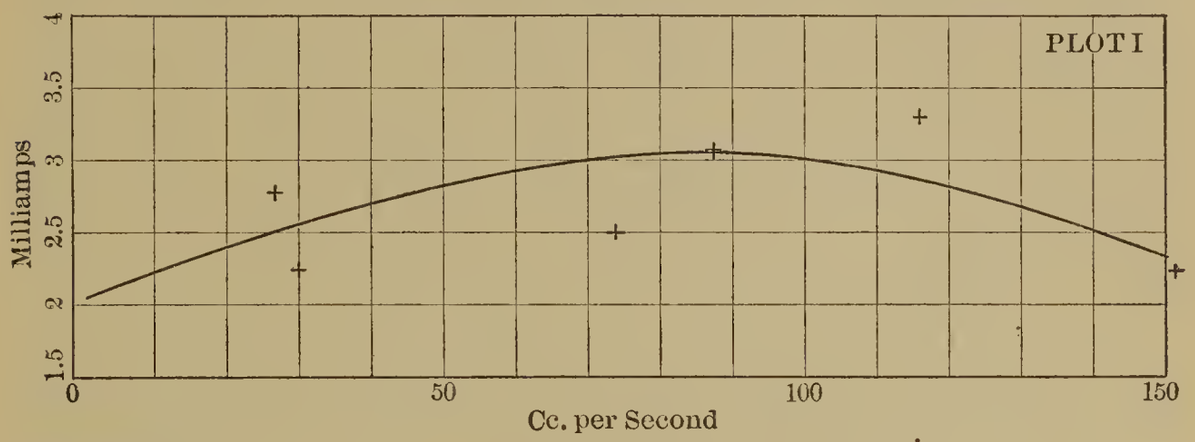
3. In the atmospheric corrosion of most electropositive metals the catalytic effect of the surface on the hydrogen-oxygen reaction, *i. e.,* upon the depolarization, seems to determine the rate of reaction.

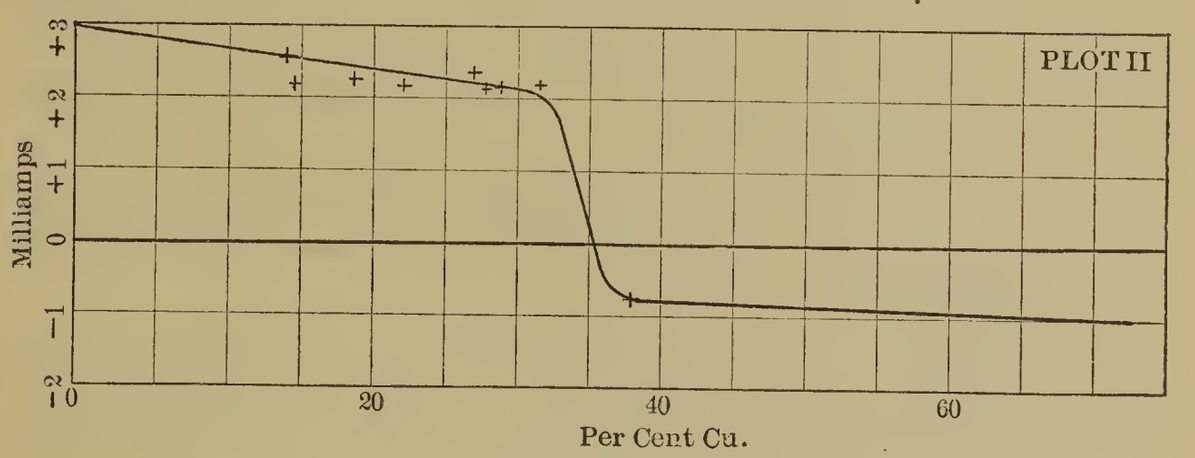
The influence of one metal on the corrosion of another is the sum-total of these effects. The action is always accompanied by flow of current, and is proportional thereto; it is suggested to measure that current, under conditions as similar as possible to those of practice. While it is not claimed that these figures have theoretical significance, they can, with proper attention to detail, be given distinct value for purposes of comparison. The size of the electrodes must be uniform, especially that of the electronegative metal, as the depolarization and hence the current is proportional to its area. The distance between the electrodes, the concentration of the electrolyte, the resistance of the external circuit, and the temperature, must be kept constant. In a short time the surface of the electronegative metal becomes coated with hydroxide which has migrated thither from the other electrode, and which cuts down the current, due perhaps to the ohmic resistance introduced, perhaps to poisoning of the catalysis. The electrodes must be freshly cleaned before each reading. The air supply is important, as the electropositive metal rapidly exhausts the oxygen from the water about the other electrode, necessitating constant replenishing.

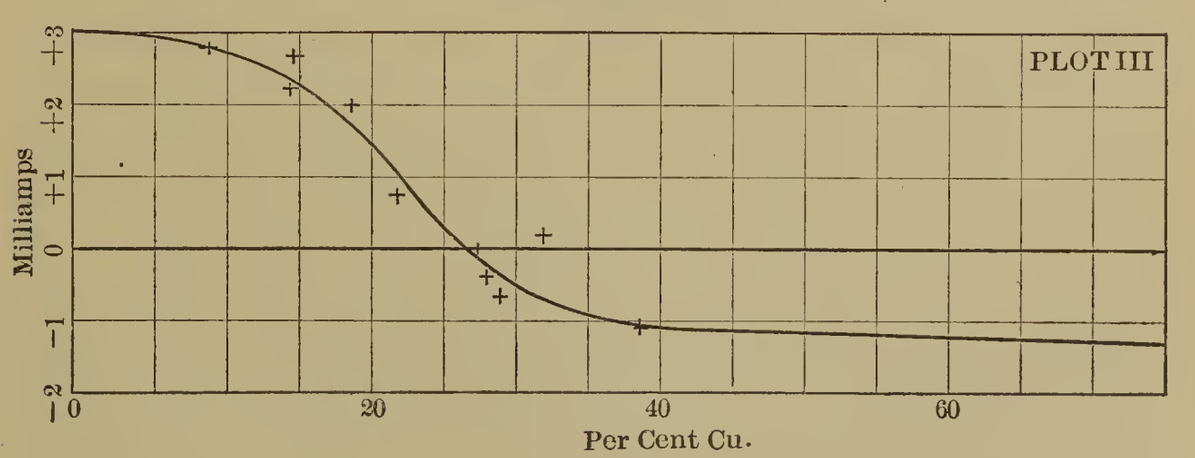
The above points are well illustrated in the case of zinc and iron. The electrodes used were rods ½ inch (1.25 cm.) in diameter with an exposed surface 1 inch (2.5 cm.) long. They were immersed in a normal KCl solution to a distance of 2 inches (5 cm.). The current, when above one milliampere, was measured by an ammeter of 30 milliampere scale deflection and 10 ohms internal resistance, while below this limit an instrument of a total range of 1 milliampere, and of 100 ohms resistance was employed. We did not have at our disposal two instruments of suitable range, of equal resistance. That the influence of resistance was small is shown by the fact that for currents below one milliampere the introduction of an additional one hundred

ohms changed the current by less than one-tenth unit. These arbitrary standards were fixed after preliminary tests, for the sake of uniformity in these respects.

When fresh electrodes are immersed there is a strong first swing of the galvanometer, the reading decreasing rapidly, and







then more slowly. After from two to four minutes the rate of diminution, though never zero, becomes very small. The magnitude of the first swing is probably determined by the potential difference between the electrodes, the closing of the circuit offering a fresh area for the unrestricted deposition of hydrogen.

The current is rapidly reduced by polarization, and soon reaches a fixed value representing equilibrium between hydrogen deposition and the diffusion to the electrode of the oxygen necessary for its depolarization. This current is the value we propose to use. In a short time there is in addition, as we have already stated, a deposition on the depolarizing surface of hydrate from the other electrode, the ohmic resistance is increased and the current continues to fall. All values in this article were taken at the end of the first rapid drop. Washing and wiping the depolarizing surface is sufficient to reproduce the phenomena and the readings. The experimental accuracy obtained is indicated by the deviation of the individual observations from the curves.

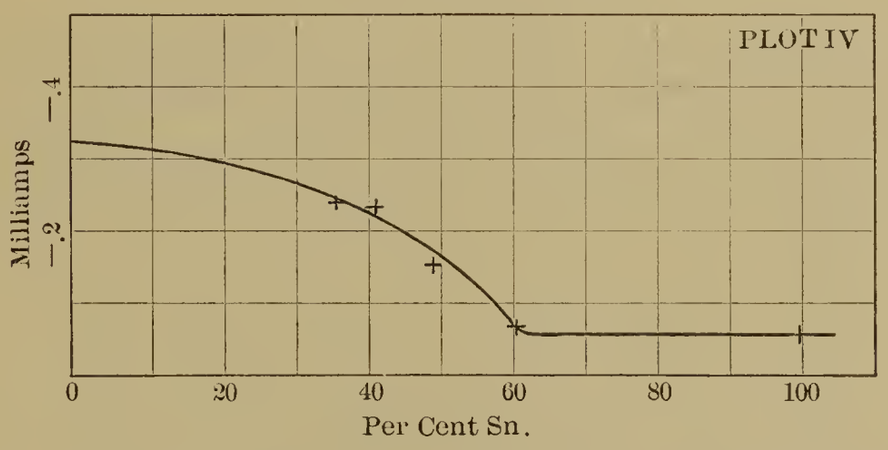
To show the influence of the air supply on the current obtained, measurements were made with zinc and iron electrodes, varying the amount of air bubbled about the iron. The results are shown in Plot I. The current rises distinctly with increase of air up to a definite maximum, beyond which it begins to fall. The decrease is probably due to the high resistance introduced into the circuit by the lack of continuity of the solution when excessive air is used. For our further work the rate approximated one hundred cubic centimeters per second.

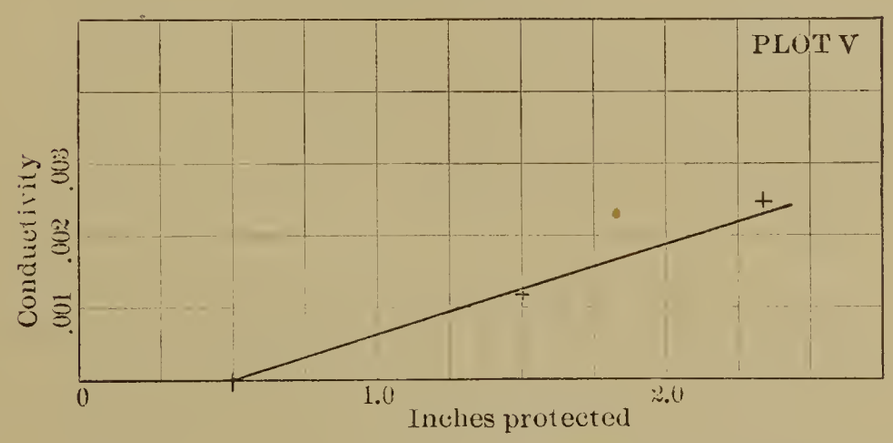
To illustrate the utility of the method, tests were made of the action of alloys of zinc and copper on the corrosion of iron. The results are shown in Plot II. The runs were further continued, and at the end of a week the values shown in Plot III were obtained. All alloys containing appreciable amounts of copper have decreased in protective capacity, those above twenty percent of copper which were at first as strongly protective as zinc itself having already so completely lost their surface zinc that they have become electronegative to iron and accelerate its corrosion. All of these alloys have become distinctly red in color. On re-surfacing with emery, the original values were obtained. These facts emphasize the point that the protection of a metal by one more electropositive is always at the expense of the latter. Iron under water in contact with zinc will be protected over an area depending on the conductivity of the water so long as the zinc remains,[1] but iron in contact with brass will be protected a

[1] If a steel sheet with a zinc button riveted to its center be immersed in water in the presence of air, the radius protected is approximately a straight line with the conductivity of the water, as shown in Plot V. The electrolyte used was KCl.

very short time, the length of which depends on the percent of copper, after which its corrosion will be accelerated. The relative periods of protection can be determined from the variation of the depolarizing current with the time, as shown above.

To further show the applicability of the method, the data shown in Plot IV were obtained for the alloys of tin and lead. Terne-plate is claimed to resist corrosion better than tin. These figures prove that lead accelerates the corrosion of iron far more than tin, and that lead-tin alloys accelerate increasingly with the





proportion of lead. If terne-plate be really the more resistant, it must be on account either of the smaller number of pin-holes, due to better adhesion of the coating, or of a different structure of the holes themselves, which interferes with corrosion. It seems more likely that the pin-holes, while fewer in number, corrode more rapidly in terne-plate than in tin. Moreover, the results indicate that, other things equal, the terne-plate containing the least lead necessary to reduce the number of holes to a minimum, will most successfully resist corrosion.

This article has shown the utility of the determination of the

depolarizing current as a measure of the influence, under atmospheric conditions, of one metal on the corrosion of another.

This test is of importance in determining the relative effects of various alloys on the corrosion of the iron and steel with which they are to be in contact in construction exposed to moisture.

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Boston.

DISCUSSION.

MR. F. N. SPELLER: The authors do not say anything as to the influence of different surface finishes. Where iron and steel products are being tested as to the difference in potentials it is very important to know just what the condition of the surface happens to be.

DR. WM. H. WALKER: These, I am quite positive, were emery-cleaned.

MR. SPELLER: We have been using a similar system of testing the effect of surface finish on difference of potential between steels with satisfactory results; the aeration of the electrolyte tends to maintain a steady difference of potential, thereby making comparative determinations possible. I call your attention to the words "most electro-positive metals" because it appears that the copper steels which have been recently developed, some of which have a very low rate of solution, are an exception to the general proposition stated by the authors in section 3. It seems in this case that the rate of solution of the iron controls the rate of corrosion, this being apparently slower than the hydrogen-oxygen reaction.

DR. W. K. LEWIS (*Communicated*): Preliminary work in this laboratory proves that the slow corrosion of copper steels is due, in some electrolytes at least, not to a change in potential of the steel, as suggested by Mr. Speller, but almost wholly to the reduction of the cathodic depolarization. In other words, copper in steel poisons the catalysis of the hydrogen-oxygen reaction. The exceptions referred to by the authors were such metals as aluminum, where the polarization is anodic, perhaps due to an oxide coat.

A paper presented before the Section: "Electrochemistry" of the VIII International Congress of Applied Chemistry, in New York City, September 12, 1912, Mr. F. A. Lidbury in the Chair.

THE ELECTRO-ANALYSIS OF COPPER, ANTIMONY, BISMUTH AND TIN WITH ACIDIFIED CHLORIDE ELECTROLYTES.

By Eugene P. Schoch and Denton J. Brown.

Solutions of chlorides of metals acidified with hydrochloric acid have been heretofore considered to be unsuitable for the electro-analytical depositions of metals, probably on account of the oxidizing effect of the liberated chlorine. Since the liberation of chlorine can be prevented by the addition of a reducing agent, and since such electrolytes present all the advantages of *simple, acid electrolytes* desirable for electro-analytical work, while in many respects they are more serviceable or convenient than either the nitric-acid or the sulphuric-acid electrolytes advocated by Foerster[1] and by Sand[2], we decided to investigate their use, particularly with metals such as copper, antimony, bismuth, and tin, for which hydrochloric-acid electrolytes are generally considered to be unsuitable, and for two of which,—namely, antimony and tin—the use of any simple acid electrolyte cannot be said to have been made *practicable* even by the recent excellent work of Sand.[3]

We have found that copper, antimony, bismuth, and tin may be deposited quantitatively and in good form from hydrochloric-acid electrolytes if suitable reducing agents (formalin, hydroxylamine hydrochloride, oxalic acid, etc.) are added to them. By these means we have found it possible to separate copper from tin and determine both from the same sample of electrolyte, thus reducing the otherwise troublesome analysis of bronze[4] to a very simple operation; and we have found that metals with a potential more positive than that of tin do not interfere with the determination of copper by this method.

[1] "Elektrochemie Waesseriger Lösungen," page 235. See also, Zeitsch. angew. Chem., **19**, 1842 (1906).
[2] J. Chem. Soc. **91**, 401 (1907).
[3] *Ibid*, **93**, 1573 (1908).
[4] Z. Elektrochem., **15**, 591 (1909).

The essential fact that makes this electrolyte serviceable is the presence of the reducing agent. Very probably, the deposition of the metal takes place by the discharge of the lower valence

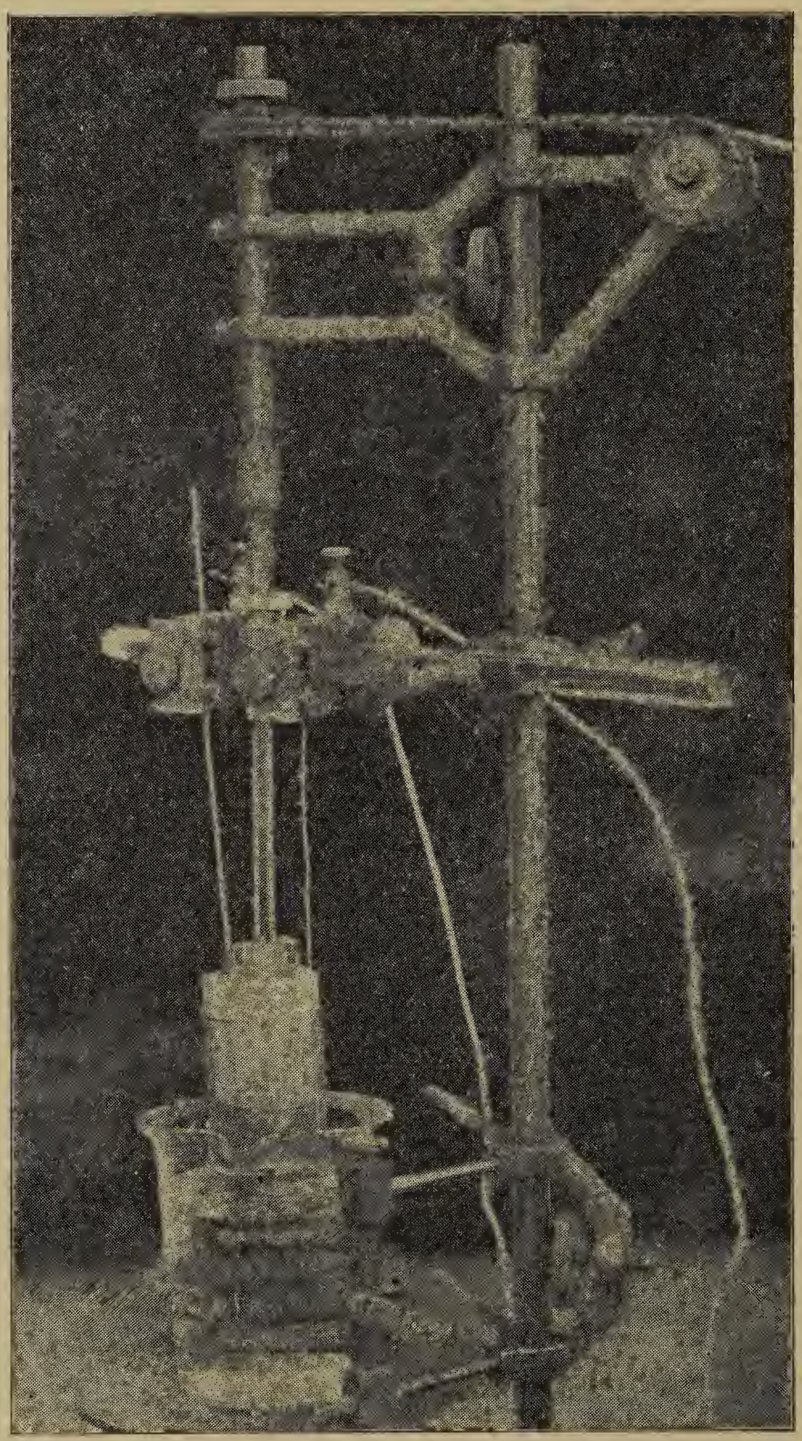

FIG. 1.

ions, and the reducing agent serves, in effect, to change the higher valence ions to the lower valence ions.

These methods present many advantages over older methods. The electrolytes are easily prepared, because all of the metals

are soluble in aqua regia, and all of their compounds are soluble either in this reagent or in hydrochloric acid. These electrolytes are free from odor as compared with the sulphide electrolytes frequently used for antimony and tin. The results indicate that the deposits obtained are probably free from inclusions; and the time required for the determinations characterizes these methods as "rapid" methods.

The experimental details and the results obtained are presented below under suitable headings. Further work along this line is in progress.

The Electrolytic Apparatus

All the work in this paper was done with the special form of Sand[5] electrodes designed by A. Fischer.[6] The only change made was in the manner of clamping the electrodes. This was modified so that either electrode could be removed without disturbing the other, and that after removal they could easily be replaced in the same position. This new arrangement also makes the assembled apparatus more rigid than before. For this purpose, two special clamps,[7] held by a glass rod, are placed on opposite sides of the stirrer to hold the electrode connecting rods which extend straight up from the concentric wire-gauze cylinders (the electrodes). The arrangement is shown in the accompanying figure. The rods are clamped in a V-shaped groove by a blunt-edged wedge, 3 cm. in length, and the wedge is fixed so that it moves straight in or out of the groove. Thus the platinum rods are gripped firmly, but without being injured.

The stirrer was turned at a rate of 800-1000 revolutions per minute.

We have found this electrolytic apparatus extremely serviceable. The platinum electrodes are relatively light; the outer cylinder weighs about 15 grams, and the inner cylinder about 13 grams, which shows that they compare very favorably in price with any other form of electrodes used for this purpose.

[5] J. Chem. Soc., 91, 374 (1907).

[6] "Elektro-Analytische Schnellmethoden" (F. Enke, Stuttgart), page 78, or Z. Elektrochem., 13, 469 (1907). The apparatus and electrodes we used were made by Fritz Koehler, Leipzig. They are shown in his catalogue, Nos. 6092 and 6100.

[7] This special clamp, as designed by one of us, can be obtained from Fritz Koehler (Catalogue No. 6205).

The Determination of Tin.

Preliminary experiments showed that, in the absence of a reducing agent, the greater part of tin present in a solution of stannous chloride acidified with hydrochloric acid can be deposited rapidly in good form, but that a remnant cannot be deposited even though the current is continued for a long period of time. However, when a suitable reducing agent is present, the metal is deposited *quantitatively*.

In all the determinations, the weighed quantities of "Baker's Analyzed" pure tin were dissolved, cold, in approximately 10 c.c. of hydrochloric acid, sp. gr. 1.20. The tin dissolved in a few hours if placed in contact with platinum. The resulting solutions were diluted to approximately 200 c.c., at which concentration they were subjected to electrolysis. The reducing agents were added in the form of pulverized solids or in the form of concentrated solutions, so that their addition did not affect the concentration materially.

The *maximum current density* with which *a good deposit* of tin may be obtained out of the hydrochloric-acid electrolyte *decreases as the concentration of the tin salt increases.* With amounts of tin as high as 0.7 gram in 200 c.c., a current of 1.5 amperes gave us with our electrodes a good deposit at all temperatures at which we worked, *i. e.*, 30° to 70°C. With higher current densities, such relatively concentrated solutions gave granular deposits, but with solutions of lesser concentration good deposits may be obtained with somewhat higher current densities. As 0.7 gram would be as large an amount of tin as would ever be used in an analysis, and as 1.5 amperes could hence be safely used in any case, we have used a current of 1.5 amperes in all our determinations.

The results obtained with different reducing agents will now be considered.

When hydroxylamine hydrochloride is present in the hydrochloric-acid electrolyte, tin is deposited quantitatively in a short period of time. The results obtained are given in Table I.

When formalin is present, the deposition of tin is incomplete, but more complete than without a reducing agent. This is surprising because in some respects formalin is a stronger reduc-

ing agent than hydroxylamine. It may be due to the fact that formalin acts as an oxidizing agent towards energetic reducing agents.

When oxalic acid is present in the hydrochloric-acid electrolyte, tin is deposited almost, but not quite, completely, as the figures in Table I show.

TABLE I.

Tin Used (Grams)	Reducing Agent	Time (Minutes)	Tin Deposited (Grams)
0.4370	4 grams NH_2OH, HCl	95	0.4380
0.2460	"	90	0.2466
0.6972	"	90	0.6970
0.3046	"	120	0.3052
0.3000	"	120	0.3000
0.3580	10 grams Oxalic Acid	75	0.3572
0.3830	"	75	0.3822
0.2070	"	85	0.2064

As is well known from Classen's ammonium oxalate method, tin may be completely deposited out of an electrolyte to which both ammonium oxalate and oxalic acid have been added. Classen's method thus appears as a special example of our general method. However, the oxalate methods heretofore employed have some undesirable features; the procedure recommended by Classen gives an excellent deposit, but requires a long period of time (nine hours); while Exner's rapid method requires the use of a "hot saturated" solution of ammonium oxalate, which is somewhat troublesome to handle, and the deposit obtained is loosely adherent and powdery. Hence an improvement of the oxalate method is desirable, and since we have found that the maximum current density with which a good deposit of tin may be obtained from this oxalate electrolyte *increases* as the concentration of the tin *decreases,* we concluded to combine this principle with the fact stated at the opening of this section on the "Determination of Tin." Thus we obtained the following method:

The greater part of the tin is deposited rapidly out of the simple hydrochloric-acid electrolyte without a reducer, and then ammonium oxalate and oxalic acid are added and the remnant

of tin is deposited *fairly rapidly*. By these means an excellent deposit of tin is obtained in about 90 minutes, which places the method in the list of rapid methods. The results we have obtained with this method are presented below in Table II.

The table shows that the temperature range within which tin can be deposited by this method extends up to 70°C. At 75°, the tendency of the stannic salt to hydrolize becomes so great as to render this method impracticable.

TABLE II.

Tin Used (Grams)	Temp.	Time I (Minutes)	Oxalate Added (Grams)	Oxalic Ac. Added (Grams)	Time II (Minutes)	Total Time	Tin Deposited (Grams)
0.3112	50–60°	45	4	10	45	90	0.3114
0.3088	"	45	7	18	45	90	0.3092
0.3157	"	60	7	18	45	105	0.3156
0.3542	"	60	7	18	45	105	0.3537
0.4852	"	75	7	18	45	120	0.4849
0.6838	"	80	10	18	55	135	0.6834
0.3550	"	45	7	16	45	90	0.3550
0.2675	"	45	7	17	45	90	0.2674
0.2608	"	45	4	10	30	75	0.2606
0.3110	30–35°		Not Weighed	Not Weighed		120	0.3114
0.3862	"		"	"		120	0.3862
0.3482	"		"	"		120	0.3479
0.3816	"		"	"		120	0.3809
0.5964	"		"	"		150	0.5958
0.3862	60–70°		"	"		120	0.3864
0.4506	"		"	"		120	0.4506
0.4670	"		"	"		120	0.4667
0.6944	"		"	"		150	0.6944

In Table II, the column under "Time I" shows the number of minutes during which the *original* hydrochloric acid solution was electrolyzed, and "Time II" shows the number of minutes during which the solution was electrolyzed after the addition of ammonium oxalate and oxalic acid.

The Determination of Copper and Its Separation from Other Metals.

It is impossible to deposit copper in good condition from a simple solution of cupric chloride acidified with hydrochloric acid, but in the presence of hydroxylamine hydrochloride, formalin, or

—less suitably—tartaric acid, copper can be deposited quantitatively. The highest cathode potential with which copper may be obtained in good form is approximately —0.60 volt against the "normal" calomel electrode.[8] This is approximately the potential with which hydrogen begins to be evolved from this electrolyte on the copper deposit, and the appearance of hydrogen may therefore be used as an indication that the applied voltage is too great. The determinations marked "hydrogen limit" in Table III below have been made in this way, *i. e.*, by keeping the current and voltage just low enough to avoid the evolution of hydrogen. Copper may also be completely deposited with a cathode potential as low as —0.40 against the "normal" calomel electrode—a fact that makes possible the separation of copper from tin. And finally, its deposition may also be controlled by limiting the total applied voltage, as was done in Experiments 34, 35 and 36 in Table III.

Kahlbaum's electrolytic copper was used for the determinations below. It was dissolved in aqua regia, and the solution evaporated to dryness or far enough to expel the free chlorine and oxides of nitrogen, etc. An amount of hydrochloric acid which varied from 5 to 25 c.c. (sp. gr. 1.20), and the reducing agents, were then added; the solution was diluted to about 200 c.c., and subjected to electrolysis.

As the results in Table III show, copper is readily separated from tin and from all metals more positive than tin. For its separation from cadmium, nickel, cobalt, chromium, and manganese we found that tartaric acid could be used, although this reducing agent appears to us to be the least suitable for the deposition of copper, and hence formalin or hydroxylamine would do as well; but for its separation from iron, tartaric acid was found to be unsuitable, and hence hydroxylamine hydrochloride was used. For the separation of copper from tin, only hydroxylamine was used.

Special attention should be here called to the fact that the observing and limiting of the cathode potential for the quanti-

[8] For a description of the method of measuring electrode potentials with this electrolytic apparatus, see Smith, *Electro-Analysis*, fourth edition, pages 274-282. The algebraic sign in front of the volts designates the polarity of the measured electrode in the cell formed between this electrode and the auxiliary (the normal calomel) electrode. In the above example, the gauze cathode is the negative pole of the cell composed of this electrode together with the calomel electrode.

tative deposition of a metal furnishes the operator a reliable, automatic indication of the end point; as the amount of the metal in the solution approaches, and finally becomes, zero, the operator finds it necessary to reduce the applied voltage so that the current finally becomes zero (or retains a low, constant value). The end points of the determinations in Table III were ascertained in this way. This accounts for the differences in the

TABLE III.

Number of Exp.	Copper Used (Grams)	Other Metals Present	Reducing Agents	Volts Applied	Amperes	Cathode Control (Volts)	Time Min.	Copper Deposited (Grams)
1	0.2700	None	10 cc. formalin 40% sol.	1. -1.6	3 - .05	—0.40	45	0 2698
2	0.3772	"	"	1. -1.6	3 - .05	"	50	0.3770
3	0.3084	"	"	2.0 -1.6	4 - .05	"	30	0.3080
4	0.3962	"	"	2.0 -1.6	4 - .05	"	30	0.3960
5	0.5194	"	10 grams Tart. Ac.	2.0 -1.5	7.0-0.0	"	180	0.5196
6	0.3292	"	"	2.3 -1.3	8 -0	"	70	0 3298
7	0 3785	"	"	2.1 -1.5	7 -0	"	150	0.3780
8	0.3642	"	"	2.1 -1.5	6 -0	"	70	0.3650
9	0.4624	Ammonia	"	2.1 -1;5	7 -0.1	"	130	0.4616
10	0.3000	"	"	2.0 -1.5	6 -0.1	"	160	0.2995
11	0.4320	Sodium	"	2.2 -1.5	7 -0	"	75	0.4316
12	0.3411	Potassium	"	1 9 -1.5	4 -0	"	140	0.3412
13	0.5520	"	"	1.8 -1.5	3 -0	"	180	0.5510
14	0.5650	Cadmium	"	2.3 -1.5	6 -0	"	60	0.5640
15	0.2535	Nickel	"	1.9 -1 5	4 -0	"	85	0.2528
16	0.5120	Cobalt	"	2.0 -1.5	4 -0	"	60	0.5118
17	0.5072	Chromium	"	2.0 -1.5	4 -0.1	"	180	0.5070
18	0.5618	"	"	2.1 -1.5	6 -0	"	205	0.5612
19	0.4222	Manganese	"	2.0 -1.5	4 -0.3	"	190	0.4222
20	0.7342	None	2 grams NH_2OH, HCl	2.1 -1 2	6.5-0	"	30	0.7328
21	0.6136	"	"	2.8 -1.4	7 5-0	"	30	0.6139
22	0.2922	"	"	2.0 -1.2	4 -0	"	20	0.1918
23	0.3552	"	"	2.0 -1.2	4 -0	"	15	0.3548
24	0.4016	"	"	2.0 -1.2	5 -0	"	15	0.4015
25	0.4624	Iron	"	1.6 -1.3	4 -0.5	"	50	0.4622
26	0.4232	None	"	2.5 -1.0	10 -0	—0.60	10	0.4230
27	0.4094	"	"	2.4 -1.65	8 -0	"	25	0.4100
28	0.4006	"	"	2 2 -1 65	7 -0.1	"	35	0.4000
29	0.3426	"	10 cc. formalin 40% sol.	2.35-1.65	8 - .2	"	20	0 3426
30	0.6320	"	"	2.5 -2.0	10 -0.1	"	45	0.6318
31	0.4378	"	"	1.8 -1.4		Hydro. Limit	45	0.4374
32	0 2598	"	"	1.8 -1.6	2 - .05	"	50	0.2598
33	0.2880	"	2 grams HN_2OH, HCl	1.6 -1.2	2 - .05	"	00	0.2882
34	0.4388	"	"	1.5 -1 6		None	25	0.4392
35	0.4640	"	"	1.5 -1.6		"	45	0.4638
36	0 6436	"	"	1.5 -1.6		"	50	0.6434
37	0.3485	Tin	"	1.6 -1.5	3 -0	—0.40	30	0.3486

length of time required for the different determinations; and it was on account of the greater length of time required for the deposition of copper in the presence of tartaric acid than in the presence of formalin or hydroxylamine hydrochloride that we considered tartaric acid to be the least suitable reducing agent.

The separation of copper from weighed quantities of tin, and the subsequent determination of the latter, was also tested, with the results given below. After removal of the copper by the

method given above, the tin was determined by our "modified oxalate" method, because these determinations were made before we found that tin could be determined more readily by means of hydroxylamine.

Copper		Tin	
Used (Grams)	Deposited (Grams)	Used (Grams)	Deposited (Grams)
0.5165	0.5165	0.6126	0.6147
0.4502	0.4482	0.3148	0.3162
0.3334	0.3344	0.2124	0.2120
0.5002	0.5004	0.5002	0.5008
0.5002	0.5006	0.5860	0.5858

The analysis of an alloy of copper and tin (bronze) is thus reduced to the following simple procedure: Dissolve the alloy in aqua regia, evaporate the resulting solution to expel the free chlorine and oxides of nitrogen, add 2 grams of hydroxylamine hydrochloride and from 5 to 15 c.c. of hydrochloric acid, sp. gr. 1.20, and water sufficient to make the total volume about 200 c.c. Electrolyze with the Sand-Fischer electrodes, limiting the cathode potential to —0.40 volt against the "normal" calomel electrode. The copper will be completely deposited in from 20 to 40 minutes, and the "end point" will be recognized by the fact that the current will have to be reduced to zero to prevent the cathode potential from rising above the limiting value. Lower the beaker away from the electrode, and wash the latter with a jet of water, catching the wash water in the beaker containing the electrolyte. The amount of water required for this purpose will be only a few c.c., which will not increase the volume of the electrolyte materially. The cathode is detached, dipped in alcohol and in ether, dried high above a flame, and weighed immediately. Since this electrode is copper plated, it may be used immediately for the deposition of the tin. Another portion of 3 grams of hydroxylamine hydrochloride is then added, and the solution is electrolyzed again with a constant current of 1.5 amperes. From 20 to 40 minutes will be required to deposit the tin. The end point may be ascertained by means of hydrogen sulphide.

The Determination of Antimony.

In the determination of antimony from acidified chloride solutions, several peculiar properties of its salts must be considered. If hydrogen is evolved during the electro-deposition of the metal, some of the latter will be lost in the form of stibine. If the electro-deposition takes place at temperatures below 50°C., the impure "explosive" antimony is deposited.[9] At temperatures above 50°C., the tendency of the solutions to hydrolyze increases rapidly and is decidedly marked; and if the pentachloride is present, it will volatilize appreciably at these higher temperatures. The following procedure was designed to avoid errors arising from any of these causes.

Weighed samples of antimonious oxide, Sb_2O_3, "Baker's Analyzed," were treated with 20-25 c.c. of hydrochloric acid, sp. gr. 1.20, and with 2 grams of hydroxylamine hydrochloride. The resulting solution was diluted to 200 c.c., heated to a temperature between 50° and 75°C., and electrolyzed with the cathode potential limited to —0.40 volt against the "normal" calomel electrode. The following results were obtained:

Sb_2O_3 Used (Grams)	Antimony		Time (Minutes)
	In Sample (Grams)	Deposited (Grams)	
0.6990	0.5825	0.5814	15
0.4390	0.3658	0.3647	10
0.5542	0.4618	0.4600	10
0.2456	0 2047	0.2048	8
0.4708	0.3923	0.3928	15
0.4844	0.4038	0.4044	5

The Determination of Bismuth.

In order to obtain a good deposit of bismuth out of a hydrochloric-acid electrolyte to which hydroxylamine hydrochloride has been added, it was found necessary to limit the cathode potential to —0.25 volt (against the "normal" calomel electrode) until most of the metal had been deposited, and then, to deposit the last portions, the voltage had to be raised gradually until

[9] Z. phys. Chem., **52**, 129 (1905).

the cathode potential was —0.60 volt (against the "normal" calomel electrode) during the last few minutes before the current was interrupted.

"Baker's Analyzed" pure oxychloride of bismuth was used for the following determinations. The samples were dissolved in 5 c.c. of hydrochloric acid (sp. gr. 1.20), 2 grams of hydroxylamine hydrochloride were added, the solution was diluted to 200 c.c., heated to a temperature between 55° and 75°C., and subjected to electrolysis in the manner stated above. The following results were obtained.

BiOCl Used (Grams)	Bismuth		Time (Minutes)
	In Sample (Grams)	Deposited (Grams)	
0.3726	0.3012	0.3006	20
0.3650	0.4568	0.4564	12
0.3666	0.2964	0.2956	32
0.3346	0.2705	0.2700	25
0.4764	0.3852	0.3852	20

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THE CO-PRECIPITATION OF COPPER AND CARBON BY ELECTROLYSIS.

By Ellwood B. Spear, C. Chow and A. L. Chesley.

Carbon has been found by Lambris in the deposit obtained by electrolyzing iron and nickel solutions,[1] but we have not discovered any reference in the literature to the presence of carbon in electrolytic copper. In fact Lambris states definitely that carbon is not precipitated at the cathode with copper under the same experimental conditions with which it is found in nickel deposits. We have succeeded in proving that carbon is precipitated at the cathode during the electrolysis of a copper sulfate solution containing a little nitric acid and a small amount of gelatin.

Experimental Conditions.

Copper Sulfate Solution.—60 grams of pure blue vitriol were dissolved in water and made up to one liter.

Gelatin Solution.—One gram of gelatin was allowed to soak over night in water, gently warmed until solution was complete and made up to 100 c.c. The gelatin should be of the best quality in order to obtain good results.

Solution for Electrolysis.—To 25 c.c. of the solution of copper sulfate the desired amount of nitric acid and gelatin were added and the solution made up to 100 c.c.

Electrodes.—The cathode was generally a rotating platinum crucible. Highly polished iron, brass or copper rods serve very well. Good results are more difficult to obtain with stationary electrodes. The anode was either platinum or copper. The latter was chosen when it was desirable to keep the concentration of the copper constant.

[1] Lambris, Zeit. fur Elektrochemie, **15**, 973.

Duration of Electrolysis.—The electrolysis was often continued until all the copper had been precipitated. Generally, however, the process was interrupted after about ten minutes.

Further experimental conditions of a few of our electrolyses are given in the following table:

TABLE I.

No.	cc. Gelatin	Amperes per sq. dm.	cc. HNO_3 (1 : 2)	Appearance and Structure of Deposit
1	0.0	3.6	1	Crystalline deposit, adhered well to cathode.
2	0.2	3.6	1	Good smooth deposit, dull in lustre.
3	1.0	3.6	1	Smooth, very shining deposit.
4	0.2	3.6	2.5	Good shining deposit.
5	0.5	3.6	2.5	Shining deposit, deep copper red.
6	1.0	3.6	2.5	Good shining reddish-black deposit.
7	2.0	3.6	2.5	Shining black deposit, peeled on drying.
8	4.0	3.6	2.5	Deposit fell off the cathode.
9	3.0	5.0	3.0	Beautiful shining dark red deposit.
10	3.0	10.0	3.0	Deposit peeled.
11	10.0	5.0	3.0	Dark dull deposit peeled.

Numbers 9 and 10 were carried out with a freshly prepared solution of very good gelatin.

From the above table it will be seen that if either the current density or the concentration of the gelatin becomes too high the deposit peels off the cathode during the electrolysis or afterward while the deposit is being dried. A great deal depends upon the gelatin. Some samples have no effect on the deposit until the electrolysis has been carried on for several minutes.[2] Other samples will not give a good deposit under any circumstances.

If the nitric acid is too dilute the gelatin has no effect on the character of the deposit. If the concentration is increased beyond that employed in the table the deposits are no longer black but copper colored, if increased too much there is no deposit formed unless the current density is also increased.

In order to determine whether or not the deposit contained gelatin or some of its decomposition products, about two grams of the black substance that had peeled off the cathode were

[2] Wen and Kern, Trans. Amer. Electrochemical Soc., 20, 153 (1911).

heated in a current of oxygen freed from carbon dioxide by bubbling through a strong solution of potassium hydroxide. From the heated deposit the gas was led into a solution of barium hydroxide. A white precipitate was formed, showing that the original deposit must have contained carbon either in a free or combined state. The carbon dioxide might come, of course, from the gelatin that had been precipitated with the copper.

Some of the black deposit was treated for a long time with strong ammonium hydroxide in the presence of air. A very fine black substance was left that on drying resembled lamp-black. Furthermore, several smooth shining black deposits were dissolved separately in a solution of cupric and potassium chlorides. The resulting solution when filtered cold did not leave any black residue on the filter paper. If the solutions were boiled before filtering a black residue was left that could not be dissolved in hydrochloric or dilute nitric acid. The solution of the chlorides alone when boiled and filtered left no residue. This would indicate either that the carbon was in a colloidal state when the deposit was first dissolved in the chlorides or that the carbon was in a combined state and was set free by the boiling process.

In order to determine whether or not the anodic processes had any influence on the precipitation of carbon with the copper, the cathode was enclosed in an unglazed porcelain cell. The deposits obtained even during the first minute or two did not differ in the slightest from those where the cathode was not enclosed.

Theoretical Considerations.

There are several theories for the precipitation of carbon at the cathode. Foerster[3] regards the phenomenon as a physical one, in which the carbon assumes the colloidal form and is thrown down with the metal. Verwer[4] believes that carbon dioxide on reduction gives the free carbon, while Lambris[5] has shown that either carbon dioxide, carbon monoxide or acetylene may cause the deposition of carbon at the cathode.

[3] Zeit. fur angew. Chemie, **19**, 1847 (1906).
[4] Chemiker-Ztg., **25**, 792.
[5] *l. c.*

Our experiments do not enable us to definitely conclude whether the carbon goes into the deposit because of primary or secondary reactions at the electrode, nor whether it is there in a free or combined state. It seems probable, however, from the color of the deposit and from the fact that a black residue remains after treating the deposit with ammonium-hydroxide, that at least a portion of the carbon is free.

We have not succeeded in proving that the black deposits do or do not contain cupric oxide. The dark color may also be due in some degree to the presence of finely divided copper.

Before carbon can be set free from gelatin an oxidation must take place, and therefore assumption of oxidizing action at the cathode seems justified. This point of view is further supported by the experimental fact that carbon can be thrown down with copper only in presence of oxidizing agents. Reducing agents will completely prevent its precipitation. It can be most easily obtained when nitrous or nitric acids are present in the solution for electrolysis. A concentrated solution of nitrates also gives the black shining deposit. The oxidation is doubtless due to secondary reactions at the electrode. The investigation is being continued by the use of the ultramicroscope.

SUMMARY.

In this article it has been shown experimentally that carbon can be precipitated with copper at the cathode.

Evidence is given to indicate that at least some of the carbon is in a free state in the deposit.

It is concluded from the experiments that an oxidizing action must have taken place at the cathode. This oxidation is probably due to secondary reactions.

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THE FUNCTION OF INORGANIC ADDITION AGENTS IN THE ELECTROLYTIC DEPOSITION OF COPPER.

By Ellwood B. Spear.

Many substances, such as sodium chloride, nitric acid, gelatin, tannin, etc., have a beneficial effect on the deposit if they are added under proper conditions during the electrolysis of copper solutions. A theory for the effect of colloidal substances has been proposed by E. Mueller,[1] but a great deal of work must be done on the migration of organic colloids under the influence of the electric current before the theory can be satisfactorily vindicated.

Although attempts have been made,[2] no adequate explanation for the effect of inorganic substances has been given up to the present time. The endeavor is made in this article to explain the function of these agents and the theory advanced is as follows: All addition agents that have a beneficial effect on the deposits either dissolve copper directly or serve to keep it in solution, either in colloidal or crystalloidal form.

The metal precipitated by the current has a tendency to redissolve, and the rate at which it goes into solution will depend to a large extent on the state of division. A very bad deposit, consisting of loose finely divided metal and perhaps some oxide, will dissolve faster than a smooth deposit, because the former has a much larger surface exposed. It is an experimental fact that copper can be redissolved off the cathode during the passage of the current provided that proper relations are maintained between the strength of the current and the solvent power of the liquid in the neighborhood of the cathode. We should, therefore, according to this theory, obtain a good deposit when the conditions are such that copper in the form of extremely small particles,

[1] Zeit. fur Elektrochemie, **12**, 317.

[2] E. F. Kern, Trans. of the Amer. Electrochemical Soc., **15**, 441 (1909). Ching Yu Wen and E. F. Kern, Amer. Electrochemical Soc., **20**, 121 (1911).

i. e., of molecular or colloidal dimensions, would be dissolved by the solution faster than it could be deposited by the current, and smooth copper would be deposited faster than it could be redissolved.

Substances such as potassium chloride do not dissolve copper directly; nevertheless they have an indirect bearing on the solvent tendencies of the liquid in that they form complexes with cuprous compounds and thus aid materially in keeping copper in solution so that it may be eventually thrown down on the cathode as a smooth deposit.

Although this idea was conceived before the writer saw the article by Mueller, both these theories involve the same fundamental assumption, namely, that some particles of metal, because of some disturbing influences on the cathode, such as the evolution of a gas, become loosely deposited upon, or even completely detached from, the cathode at the moment of giving up their electric charges. These particles may grow by the union of two or more to form a colloidal suspension. If the solvent power of the liquid in the vicinity of the cathode is such that the colloidal particles, which have a large surface exposed, are redissolved and therefore again assume the crystalloid form, no bad deposit would be possible.

The theory[4] that the deposit is improved because of the reducing effect of the addition agents is untenable, for it has been found[5] that sodium nitrate or sodium chlorate in the presence of free acid give good results. Even highly polished deposits of copper may be obtained from a solution of nitric acid containing a very small amount of gelatin.[6]

According to the theory of Mueller, the beneficial effects of addition agents such as tannin or gelatin are due to the fact that these substances are protective colloids and prevent the colloidal copper particles which may be formed at the time of the discharge of the copper ion molecules from falling out of solution. If the resulting combination of the copper particle and protective colloid has a positive charge, the copper would eventually find its way to the cathode and be precipitated. The protective colloid would

[4] Kern, Wen and Kern, *l. c.*

[5] Wen and Kern, *l. c.*

[6] Spear, Chow and Chesley, these Transactions, page 277.

therefore be found in the deposit of copper on the cathode. This has been verified in many cases.[7]

The results of Kern could be explained by the theory of Mueller, on the ground that the organic substances found to have a beneficial effect are either completely or partially colloidal, serve as protective colloids for the copper particles and move in the solution toward the cathode.[8]

The inorganic substances having the most marked effect on the character of the deposit in the electrolysis of copper are nitric, hydrochloric and sulfuric acids, nitrates, chlorides of ammonia and the alkali and alkaline earth metals. Sulfates of these same cations are less efficient. The sulfates and chlorides dissolve copper in the presence of the cupric ion forming, in some cases, a complex where the copper is in the anion. A familiar example of this is in the determination of carbon in steel. The steel is dissolved in a solution of cupric and alkali chlorides. Copper is at first precipitated on the iron but dissolves later, as soon as all the iron has disappeared.

That copper redissolves in copper sulfate while the current is still going through the solution has been pointed out by Meyer in his work on the copper coulometer.[9] While equilibrium conditions could scarcely obtain during electrolysis with high current densities, there is always the tendency toward the following reaction:

$$Cu + Cu^{++} \leftrightharpoons 2Cu^{+}$$

It may be that this is a factor in the formation of a bad deposit. After the concentration of the cupric ion becomes low, small colloidal particles of copper would not be so readily redissolved and would therefore accumulate on the cathode to form a loosely adhering deposit toward the end of the reaction.

Nitric acid is the best solvent for copper in the above list and it is a significant fact in support of the theory that it is also the best inorganic addition agent for improving the character of the deposit. Nitrates are also efficient, and that they have an oxidizing action is shown in the article by Spear, Chow and Chesley[10] on "Co-precipitation of Copper and Carbon by Electrolysis."

[7] Mueller, *l. c.*
[8] Northrup and Hering, Trans. Amer. Electrochemical Soc., **10**, 35 (1906).
[9] Meyer, Zeit. fur Elektrochemie, **15**, 12; also, **15**, 65.
[10] Spear, Chow and Chesley, *l. c.*

Copper cannot be thrown out of solution if the concentration of the nitric acid is too great, obviously because the acid dissolves the deposit faster than the current can form it. We should say perhaps that the electrode potential is such that something else beside copper is liberated at the cathode. As the electrolysis proceeds the nitric acid is slowly removed by the current and the copper can be completely precipitated if the process is continued long enough.

From these considerations it should be possible to correct a bad deposit of copper by adding a little nitric acid and electrolyzing the solution for a longer time. At first the loose copper should be dissolved off the electrode and again be precipitated as smooth copper. This proved to be experimentally possible. A loose, dark, fine-grained deposit of copper was obtained by electrolyzing a solution of copper sulfate with a rotating cathode. The electrodes were removed, washed, again put in place and sufficient current turned on to give a normal current density of three amperes. A solution consisting of 2.5 c.c. nitric acid (1.42) in 100 c.c. water was then raised to cover the electrodes. The solution turned blue in a few seconds, showing that copper had been dissolved. After electrolyzing for some time the solution again became colorless, indicating that the copper had been reprecipitated. This experiment was repeated many times with varying concentrations of nitric acid. If the concentration of the acid was too great all the copper was dissolved off the cathode and none was redeposited; if it was too small there was no perceptible effect. The deposit was improved in every case where the acid was kept within the limits, 1.5—5 c.c. (1.42) per 100 c.c. solution. As nitric acid is destroyed very slowly by the current under the above conditions, these experiments show conclusively that the solution of loose copper and its redeposition in a smooth form can go on simultaneously on the cathode, which is a fundamental assumption of the theory.

It is a familiar experience in electroanalysis to have a copper deposit become loose and worthless if the current is allowed to go through the solution too long, although the deposit may have been firm and adherent when the solution first became colorless. The theory explains this phenomenon on the ground that copper

is being continuously dissolved and reprecipitated. It is dissolved off the entire electrode but is reprecipitated where the current is greatest, *viz.*, on points on the cathode nearest the anode. If an electrolytic operation with stationary electrodes is left long enough, copper will entirely disappear from the back of the cathode and be precipitated in the form of trees on the side nearest the anode.

The correction of a bad deposit by addition agents other than nitric acid is attended with results of a less positive nature than the theory demands, because they are not so good oxidizing agents and therefore do not dissolve the copper so readily. Nevertheless an 8 percent solution of ammonium or sodium nitrate turned blue when brought in contact with a bad deposit, although a normal current density of three amperes was maintained. Much more dilute solutions of nitrates will dissolve finely divided copper. It has not been ascertained whether the presence of air is essential or not.

SUMMARY.

In this article the theory is advanced that the function of inorganic addition agents in the electrolysis of copper solutions is to keep the copper in solution.

The fundamental assumptions are:

(a) That some particles of copper may assume the colloidal form at the moment of giving up their electric charges at the cathode.

(b) That oxidation may take place on the cathode during the passage of the current.

Experimental proof is given to show that copper is continuously dissolved and reprecipitated at the cathode during the electrolysis of copper solutions.

The theory explains the fact that good deposits of copper become bad if the electrolysis is continued too long.

Massachusetts Institute of Technology,
Boston.

A Paper read before Sections IX: Photochemistry, IIIa: Mining and Metallurgy, II: Inorganic Chemistry, Xb: Physical Chemistry, VIII International Congress of Applied Chemistry, New York City, September 11, 1912.

BLUE GELATINE-COPPER.

By Wilder D. Bancroft and T. R. Briggs.

Copper and the copper alloys such as brass and the bronzes lend themselves very readily to artistic decoration by means of colored superficial films or "patinas." Great as is the variety of colors which may thus be imparted to copper, nevertheless a rich and true blue patina for this metal is practically unknown. It was while seeking such a blue surface film that the electrolysis of copper acetate solutions containing gelatine was first performed by us. One gram of gelatine was dissolved in 325 c.c. of a 1 per-cent solution of cupric acetate and this mixture electrolyzed between carefully cleaned and burnished electrodes of sheet-copper. The electrolysis was continued for five minutes at a cathode (and anode) current density which varied between 0.15 and 0.45 amp./sq. dm. The process was carried out at room temperature.

The electrolysis performed, the cathode was found to be covered on its inner surface with a thin, pale brown deposit, which, when rubbed with the fingers, was seen to possess a peculiar, slippery surface caused by a very appreciable amount of gelatine deposited simultaneously with the metallic copper. No gas became visible at either pole during the passage of the current.

In itself, this pale brown cathode deposit gave no indication of its peculiar properties, and it was by chance only that these were discovered. An electrode freshly coated with a layer of the gelatine-copper was by an oversight allowed to remain in the solution of copper acetate from which the film of metal had just been deposited and the current was turned off. On removing the electrode from the solution it was noticed that the brown color originally possessed by the cathode film had given place to a purplish blue of extraordinary brilliance and beauty. This led to further experiments.

A second electrode was then coated with a film of gelatine-copper and, after careful rinsing with cold tap water, immersed in a 5 percent solution of copper acetate containing no gelatine. Straightway there ensued a remarkable series of color changes upon the surface of the copper deposit; hues of startling evenness and intensity followed each other in regular succession until the electrodes had acquired a magnificent deep-blue coloration. This process we shall speak of as a "development," since it bears a certain resemblance to the development of the silver image in the process of photography.

Experimental.

Effect of Gelatine.—After the process of development had been discovered, a more systematic study of the formation and nature of gelatine-copper was undertaken. It then became evident that gelatine must be present in the electrolyte and that this colloid exerted a tremendous influence upon the nature of the cathode deposit. The term "gelatine-copper" was thus justified. The *optimum* gelatine concentration was found to lie between 0.25 and 0.66 percent. The electrolysis of copper acetate solutions containing no gelatine failed to give the developable films, nor was it possible to substitute other hydrophile colloids such as starch or gum-arabic for gelatine or glue.

Nature of the Electrolyte.—Electrolysis of copper formate, acetate, and propionate solutions containing gelatine, resulted in cathode films which developed blue in copper acetate, although this development was imperfect in the case of the deposits from the formate solution. Copper sulphate solutions of different strengths and varying gelatine content failed absolutely to give developable deposits. Similar results were obtained with solutions of copper nitrate and chloride.

Effect of Temperature.—Variation of the temperature at which the electrolysis was performed led to interesting results. Between 20° and 40° C. the cathode deposit was of the usual pale-brown color and gave a more or less satisfactory color-development to blue in copper acetate. At 50° C. or at higher temperatures the cathode deposit was colored a bright red to a brick red and was unaffected by the developing solution. Between 55° and 60° a

short electrolysis with a low current density gave a gold-colored but very thin film which had a rather iridescent appearance. These gold and red films can be lacquered with complete success and are interesting in their application to metallochromy.

Other Factors.—The best results were obtained with copper acetate or propionate solutions made up in the proportion of 1 or 2 parts by weight of the crystallized salt to 100 parts of water. The electrolyte should be neutral or at most but very slightly acid. The current density must be low—between 0.15 and 0.45 amp./sq. dm.—and the process need not exceed 5 minutes in duration. The nature of the metal used as cathode is of little importance as long as the copper solution is not decomposed by it. Thus with nickel, brass, and platinum, good deposits were obtained as adherent cathode films which developed a good blue color.

The Development of the Blue Color.—A 5 percent copper acetate solution containing no gelatine was used as the developing bath throughout this work, although a copper propionate solution may also be employed. Copper formate developer gave less satisfactory results. A large number of other salt solutions were then tried as developers with practicably no success. Thus in normal copper sulphate solution a film of gelatine-copper was colored a dull, dark indigo. In N/50 copper sulphate a fairly-good blue color was developed, although the colors obtained with sulphate solutions are distinctly inferior to those prepared with acetate developer. Very dilute copper nitrate oxidized the film to dark brown copper oxide, while a chloride solution spoiled the deposit entirely.

Several oxidizing solutions were next used with negative results. Potassium chromate, bichromate, permanganate, perchlorate, chlorate, and persulphate failed to give even a trace of blue coloration. The films were usually oxidized slowly to brown cupric oxide. Reducing solutions gave no development. The film of gelatine-copper was unaffected by dilute, warm, hydrazine hydrate and underwent accelerated blue development in copper acetate after such treatment.

A solution of sodium acetate gave no blue coloration of the copper film, nor was it otherwise with the acetate solutions of

other metals. Hence this phenomenon must be a function of the copper contained in the developing solutions.

Reverse Development.—An electrode covered with a deep blue film was immersed in a very dilute aqueous solution of hydrazine hydrate, and in a short time bubbles of nitrogen began to form on the blue surface. The blue color then slowly faded away until, passing in the reverse direction through the series of colors previously described, the film of gelatine-copper again took on its original brown color. This process was called a "reverse development."

The reverse development completed, the electrode was rinsed in distilled water and once more immersed in the usual copper acetate developer. The blue color formed again quickly, but was a bit thin and uneven.

If a film of gelatine-copper is allowed to stand undeveloped for several hours it completely loses its power of developing in copper acetate. This is probably due to its oxidation by the air, because it was found that treatment of such a "dead" film with hydrazine hydrate was sufficient to regenerate its powers of development. The same result was obtained with a film after immersion in warm, dilute hydrogen peroxide—no development occurred until the layer of oxide so produced had been reduced with hydrazine.

Theory and Conclusions.

Schützenberger, by the electrolysis of copper acetate solutions, obtained at the cathode a peculiar form of copper; and, being unable to explain its unusual behavior, he announced it as an allotropic modification. Wiedemann incorrectly contended that the new form of copper was really the oxide of that metal, while recently Benedicks has advanced the idea that we have to deal with a solid solution of acetic acid in copper. It can be shown, however, by a careful study of their results and by consideration of the facts of colloid chemistry, that the allotropic copper of Schützenberger is merely the normal metal in the form of an irreversible colloid gel.

The same conclusion is applicable to the deposits of gelatine-copper described in this paper. The gelatine acts here as the

"protecting colloid," migrates by cataphoresis to the cathode, and there inhibits the growth or crystallization of the copper nuclei. Gelatine-copper is an irreversible gel of colloidal copper. The whole phenomenon is but another example of the marked influence of organic and other colloidal substances upon metals prepared by electrolysis, accounts of which have appeared in the recent papers of Müller and Bahntje, Snowdon, and others.

What is the nature and mechanism of the process of the color development? This is indeed a difficult problem, chiefly because of the exceeding small quantities of reacting material necessarily dealt with. The blue, although a superficial color, is nevertheless not the color of a thin film of gelatine or oxide bringing about interference disturbances in the reflected rays of light. Nor does it seem to be the color of a definite chemical compound. The blue layer does contain oxide as is shown by its action in hydrazine and yet it cannot be prepared by any process of simple oxidation. It cannot be produced by the partial coagulation of the copper gel.

It was shown by Wiedemann that Schützenberger's copper possesses the power of adsorbing very considerable quantities of copper oxide from copper acetate solutions. This observation furnished the clue to the process of development. The color changes that appear upon the film are the result of *a surface adsorption of hydrous copper oxide from the copper solution.* The hydrous copper oxide is present as a suspension in very appreciable quantities in the acetate or propionate solutions, being the product of hydrolytic dissociation. This being the case, we should expect the best development with the acetate solutions and but little color effect with the sulphate and chloride developers.

The reversal of development caused by hydrazine is due to the reduction of the adsorbed oxide. There seems to be a certain definite concentration of oxide in the copper film necessary for the production of a blue color. As the concentration of the oxide increases by continued adsorption, the film passes through the series of colors so distinctive of the development.

In conclusion it can be said in support of this hypothesis that it is in accord with many of the established facts of colloid chem-

istry and explains in the best possible manner this decidedly obscure phenomenon. Stannic oxide adsorbs gold from suspension and forms the "Purple of Cassius"; under very special conditions colloidal copper adsorbs hydrous copper oxide and similarly gives an intensely-colored adsorption compound.

SUMMARY.

The electrolytic production of a form of colloidal copper was performed with certain copper solutions containing gelatine.

This new form of copper develops a remarkable series of colors when immersed in certain copper solutions, a peacock-blue being the finest color obtained.

The process of development is an adsorption of hydrous copper oxide by the surface of the colloid film.

Methods of coloring metal objects gold, golden-brown or red have been described.

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A Paper read before Section IIIa: Mining and Metallurgy, of the VIII International Congress of Applied Chemistry, in New York City, September 6, 1912.

THE SULPHATIZING ROASTING OF COPPER ORES AND CONCENTRATES.

By Utley Wedge.

In general the art of securing copper from sulphide ores or concentrates may be said to consist of:

Separation, in the molten state, of copper sulphide with some iron sulphide, from the great bulk of gangue material followed by:

Elimination of sulphur and iron from the molten matte, by oxidation and fluxing, leaving metallic copper.

The definition is made broad enough to cover the general practice, whether or not the ore or concentrate is given a preliminary roast for the removal of surplus sulphur.

The above process, which we will designate as the smelting process, makes necessary the presence in the ore, or the addition thereto, of such silica, lime and iron as may be necessary for the formation of a light and fusible slag, together with sufficient sulphur and iron for the formation of copper matte, and also the addition to the matte of sufficient silica for the oxidation and fluxing out of the iron.

These items together with the cost of fuel sufficient for melting the mass constitute important items of cost in the copper smelting process.

Numerous cases where fluxing materials are scarce or dear, or where fuel is expensive, have caused special attention to be given recently to the wet process of copper extraction, which may be designated as consisting of forming soluble salts of copper which are then washed or leached out of the ore or concentrate by dissolving in water or acid. Metallic copper may then be secured from the solution of copper salts by electrolysis; by cementation; or, copper can be brought out of the solution as a hydroxide or other insoluble precipitate and reduced to metallic copper by subsequent melting in a reducing atmosphere.

This paper presents facts relating to only one step in the wet process of copper extraction and deals only with the formation of sulphate of copper by roasting copper ores or concentrates.

One percent of copper content requires, theoretically, one-half percent of sulphur to form sulphate of copper. In practice, it is necessary to have present an excess of sulphur over this theoretical amount. If insufficient sulphur is present in the material to be treated, it is then necessary to add sulphur in some form, either as sulphur, SO_2, SO_3, or, in the form of a sulphide or sulphate or sulphuric acid. Iron sulphides are very desirable in ores, when it is desired to sulphatize the copper values, and zinc, lead, lime and magnesia, if present in forms that will consume sulphur, are undesirable.

The principal reactions which enter into the sulphatizing of copper sulphides, are as follows:

CuS decomposes in roasting to Cu_2S + S and the free atom of S burns to SO_2 at temperatures above 350° C. (662° F.). Cu_2S at furnace temperatures below 500° C. (932° F.), reacts principally as follows:

$$2Cu_2S + 5O_2 = 2CuO + 2CuSO_4$$

At higher temperatures, the principal reaction is

$$Cu_2S + 2O_2 = 2CuO + SO_2$$

Different copper sulphide minerals behave differently at furnace temperatures, but the above formulae show the tendency common to all copper sulphides to form some quantity of copper oxide at all furnace temperatures.

In roasting to secure the highest percent of water-soluble copper, the constant formation of the copper oxide is the chief obstacle to be overcome.

The presence of iron sulphide with copper sulphide in the roasting process assists in sulphatizing the copper oxide thus formed. At furnace temperatures below 600° C. (1112° F.) there is some basic sulphate of iron formed, which, at temperatures above 530° C. (986° F.), roasts to Fe_2O_3 and SO_3 and the SO_3 gas may

combine with the CuO to form $CuSO_4$ which is practically stable at temperatures below 650° C. (1202° F.), or, the CuO may react directly with the $Fe_2(SO_4)_3$, according to the formula,

$$3CuO + Fe_2(SO_4)_3 = Fe_2O_3 + 3CuSO_4$$

Even the portion of iron sulphide which roasts to Fe_2O_3 is of some assistance in sulphatizing the CuO, as at temperatures between 500° C. and 750° C. the iron oxide acts as an energetic catalyzing agent for the oxidizing of the SO_2 to SO_3, which in turn tends to combine with the CuO to form $CuSO_4$.

Also, SO_2 generated in the furnace, either from the copper or iron sulphides, tends to sulphatize the copper oxide.

These various principles are generally familiar from enunciation by Aubell, Kothny, Ottokar Hoffman and others, and attention is called to them here to make clear the significance of the following tests made by The Wedge Mechanical Furnace Company of Philadelphia.

The following tests were made without the addition of any material to the ore treated:

Test No. 621. *February, 1910.*

Analysis of Ore.

	Percent
Cu	1.07
Fe	49.25
S	32.60
SiO	6.80
MgO	2.18
Al_2O_3	1.59

The copper present was chalcopyrite; iron present was pyrite and pyrrhotite.

Ore was roasted in a Wedge multiple hearth furnace with the following results:

Water-soluble copper	0.35% = 27.8%	extraction
Acid-soluble "	0.80% = 63.4%	"
Insoluble " "	0.11%	"
Total	1.26% = 91.2%	extraction.

The calcine from the above roast contained 4.7 percent sulphur

and was then furnaced in a Wedge multiple hearth mechanical muffle furnace. It was then leached with the following result:

Water-soluble copper	.....0.76%	= 60.3%	extraction
Acid-soluble "	.....0.48%	= 38.1%	"
Insoluble "	.....0.02%		"
Total copper secured in solution	...98.4%		"

In the above test, the copper designated as acid-soluble copper, was copper oxide, soluble in very dilute sulphuric acid.

It will be observed that in spite of the presence of liberal quantities of iron sulphide, there was considerable formation of copper oxide in the furnacing, but this occurred chiefly in the preliminary roast where, by reason of the considerable excess sulphur, temperatures became excessive. Analysis of the gas leaving the furnace in initial roasting showed formation of sufficient SO_3 for the production of sulphuric acid to recover all of the copper oxide, or if electrolysis were used in subsequent recovery of the copper from solution, more than sufficient sulphuric acid would be recovered to sulphatize the copper oxide.

Test No. 620. *March, 1910.*

ANALYSIS OF ORE.

	Percent
Cu	3.52
Fe	9.76
S	9.54
Insoluble	66.5

Copper present as chalcopyrite; gangue consisted of schist.

This ore was given a single treatment in a Wedge multiple hearth mechanical muffle furnace 9′ 9″ in diameter with five hearths; four hearths muffle-fired with coal.

The analyses made currently during the test showed:

Water-soluble copper	from 60% to 70%	of total copper	
Acid-soluble "	" 20% to 22%	"	"
Total "	80% to 92%	"	"

In this test the SO_2 and SO_3 gases generated in the upper hearths of the furnace were drawn downward over the ore on the lower hearths of the furnace. (Patent No. 966,277—August 2, 1910.)

If electrolysis were used, the sulphate of copper solution would yield in this case a great excess of sulphuric acid for the recovery of the copper oxide.

Test No. A-100. *July, 1911.*

ANALYSIS OF ORE.

	Percent
Cu	4.38
Fe	9.61
S	16.37
CaO	1.10
MgO	0.72
Insoluble	61.21

Copper present as chalcopyrite; the gangue was diabase.

This ore was given a single treatment in a Wedge multiple hearth muffle furnace (Patent No. 654,335—July 24, 1900.) having a diameter of 9′ 9″ with five hearths, being the same furnace as was used in the previous test.

Actual leaching of this ore showed a recovery by

Water extraction	73.7%	of copper in ore
Weak sulphuric acid	15.7%	" " " "
Making a total of	89.4%	of the total copper in ore.

It is believed that this ore, sulphatized in a larger furnace of the Wedge type, would yield still better results.

Tests so far given, were made with ores containing copper as chalcopyrite.

The following tests were made with an ore in which the copper was present chiefly as Bornite with some silicate and carbonate of copper.

Sample No. 125. *April, 1911.*

ANALYSIS OF ORE.

	Percent
Cu	3.40
Fe	11.05
S	13.02
SiO_2	63.90

This ore was ground to 20-mesh and was given a single treatment in a small test furnace and showed:

Water-soluble copper	80.80%	of total copper contents
Acid-soluble "	11.8 %	" " " "
Total recovery	92.6 %	" " " "

The above results have since been duplicated with this ore in a Wedge mechanical muffle furnace 20′ 0″ in diameter with five hearths and sufficient sulphuric acid is recovered from the SO_3 in gases leaving the furnace to recover the oxide of copper formed and make the extraction as above shown in the subsequent leaching operation.

Sample No. 7. *December, 1909.*

ANALYSIS OF ORE.

	Percent
Cu	1.85
Ni	2.75
Fe	47.78
S	30.85
SiO_2	15.30

It was desired to extract the copper, leaving the nickel in the leached ore, together with the iron.

The analysis of the calcine showed:

Water-soluble.....	Copper	69.2%	Nickel	13.6%
Acid-soluble.....	"	12.8%	"	4.4%
Total soluble.....	"	82.0%	"	18.0%

The leached ore contained

	Percent
Copper	0.29
Nickel	2.80

It has been shown in tests made by The Wedge Mechanical Furnace Company that copper ores containing little or no sulphur or iron can be treated by sulphatizing roasting by the addition of sulphide of iron, in the form of iron pyrites.

Test No. 604. *August, 1909.*

ANALYSIS OF ORE.

	Percent
Cu	3.14
Fe	2.25
S	none
Insoluble	85.5

This ore contained copper as carbonate and the gangue was porphyry.

This ore was mixed with 5 percent of iron pyrites containing 47.5 percent sulphur.

The test was made in a 9′ 9″ Wedge mechanical muffle furnace with five hearths and the analysis of the calcine showed 92 percent of the copper to be soluble in water. The copper solution was very pure, containing only from 0.1 percent to 0.2 percent Fe_2O_3 to 7 percent copper sulphate. Copper precipitated from the solution with clean scrap iron tested 96 percent pure cement copper.

Test No. 634. *November, 1910.*

Analysis of Ore.

	Percent
Cu	1.86
Fe	2.79
S	0.80
Al_2O_3	2.58
Insoluble	88.3
Combined water	3.4

The sulphur contained in this ore seemed to be partly in cinders from the locomotive, which accumulated in the open car during transit from the West. Copper was present largely as silicate of copper. 6 percent pyrites containing 47 percent sulphur was added to this ore and this mixture was given a single treatment in a Wedge Mechanical Furnace, muffle-fired with coal; diameter of furnace 9′ 9″ with five hearths and a preheating hearth. Tests were made of the material as it progressed through the furnace from hearth No. 1 (top hearth) and showed as follows:

Leaving Hearth	No. 1	79.3%	of copper water-soluble
" "	No. 2	81.4%	" " " "
" "	No. 3	93.4%	" " " "
" "	No. 4	95.2%	" " " "
" "	No. 5	95.2%	" " " "

There was no heat applied to the fifth hearth and the sulphatizing was completed in the fourth hearth. This calcine leached readily with cold water, using one ton of water per ton of ore. Solution secured was used on successive batches and brought up to 15 percent $CuSO_4$ containing only 0.1 percent Fe. The tailings from this leaching test contained 0.08 percent Cu.

Up to this time, very few records are available from furnaces of large size. The furnace with which most of these records were made was a furnace 9′ 9″ in diameter and 12′ high, with

five hearths and a preheating hearth. This furnace, a generation ago, would have been considered a large furnace, even with a capacity of only one carload of ore per week, but the commercial problems of today call for much larger appliances. Several large mechanical muffle furnaces are now installing by large copper companies and records from furnaces with an output of 20 tons to 40 tons daily, per furnace, will soon be available.

The above is a record indicating in advance the possibilities of a process which may soon, in special cases, displace the smelting process of copper production.

Ardmore, Pa.

A Paper presented at the XXII General Meeting of the American Electrochemical Society, in Joint Session with Sections IIIa: Mining and Metallurgy; Xa: Electrochemistry, and XIb: Conservation, of the VIII International Congress of Applied Chemistry, in New York City, September 10, 1912.

ON THE ELECTROLYTIC REFINING OF SILVER-BISMUTH ALLOYS.*

By William N. Lacey.

OBJECT.

The object of this investigation was to determine to what extent silver could be separated from bismuth by electrolysis of the binary alloys of the two metals.

NATURE OF BINARY ALLOYS OF SILVER AND BISMUTH.

Comparatively little work has been done on the binary alloys containing silver and bismuth. Laurie[1] showed that no compounds were formed in these alloys. Mathiessen[2] found that their electrical conductivity increased with an increasing silver content. The experiments of Heycock and Neville[3] show that the eutectic point is reached with a 2.5 percent silver content and with 97.5 percent of bismuth. The microscopic examination of Petrenko[4] showed that the alloys ranging from 5 percent to 95 percent silver consist of white mixed crystals, rich in silver, surrounded by gray microcrystalline masses of the eutectic. Above 95 percent silver a solid solution of bismuth in silver crystallized out on cooling. At 2.5 percent silver only the eutectic was to be found, while at 1 percent silver, bismuth crystals were found mixed with the eutectic.

WORK OF OTHERS.

Foerster and Schwabe[5] carried on experiments on the refining of bismuth in anode slimes from the Betts process for the

*A thesis presented in partial fulfillment of the requirements for the degree of Chemical Engineer at Stanford University.

[1] Journ. Chem. Soc., **65**, 1031 (1894).

[2] Ann. der Phys. und Chem., **110**, 190 (1860).

[3] Phil. Trans., 189A (1897).

[4] Zeitsch. für Anorg. Chem., **50**, 136.

[5] Zeitsch. für Elektrochemie, **16**, 279 (1910).

electrolytic refining of lead, which contained lead, silver and bismuth. They recommend the use of a solution of the fluosilicate of bismuth, $Bi_2(SiF_6)_3$, as an electrolyte. At a temperature of 18° C. this electrolyte gives an even, compact cathode deposit of bismuth for current densities from 0.4 to 1.2 amperes per 100 sq. cm., the electrolyte being slowly stirred.

EXPERIMENTAL.

I.

Three alloys were prepared by melting silver and bismuth together in a clay crucible and casting into small ingots. The compositions of these alloys as determined by analysis were as follows:

Name of Alloy	Percent of Silver	Percent of Bismuth
"A"	65	35
"B"	2.8	97.2
"C"	53	47

Alloy "A" had a fine-grained crystalline structure. It was brittle and non-sectile, although it was easily scratched by a knife point. Alloy "B" had a coarse-grained crystalline structure. It was quite brittle and sectile. The appearance of alloy "B" closely resembled that of metallic bismuth, while "A" had the white color characteristic of metallic silver. Alloy "C" was intermediate in its characteristics, as would be expected from its composition.

II.

Electromotive force determinations were made for alloys "A" and "B" in each of two electrolytes, *i. e.*, cyanide of silver and nitrate of silver, using metallic silver as the other pole of the cell. In these determinations a capillary electrometer and a Wheatstone bridge was used as explained by Ewell.[6] The results obtained are shown in the following tabulation:

Electrolyte	Positive Pole	Negative Pole	EMF of Cell—Volts
Cyanide	Alloy "A"	Silver	0.202
Cyanide	Alloy "B"	Silver	0.242
Cyanide	Bismuth	Silver	0.173
Nitrate	Silver	Alloy "A"	0.591
Nitrate	Silver	Alloy "B"	0.448
Nitrate	Silver	Bismuth	0.288

[6] Ewell, Physical Chemistry, pages 59 and 60.

The "cyanide electrolyte" was prepared by adding a 5 percent solution of potassium cyanide (KCN) to a 5 percent solution of silver nitrate ($AgNO_3$). until the precipitate dissolved. This electrolyte was used for the electrolyses of Part III, but in this case just enough of an excess of cyanide solution was added to keep any silver cyanide from forming during the electrolysis.

The "nitrate electrolyte" is the one used in the U. S. Mint at San Francisco[7] in the electrolytic refining of silver bullion. It was a solution containing 3 percent silver, as silver nitrate, and 2 percent of free nitric acid. This electrolyte could not be used for the electromotive force determinations, since the alloys became coated with a black deposit of silver when put into it, so for the purpose of determining the electromotive forces the silver nitrate was replaced by an equivalent amount of sodium nitrate.

The solution was stirred during the time these measurements were being made in order to have the conditions the same as those under which the electrolyses were carried on. Similar electromotive force determinations were made without stirring the electrolyte, giving lower values than those stated above. These results, having no direct bearing upon this work, will not be given here.

The difference in polarity of the two alloys in the two solutions is probably due to the fact that there are relatively few silver ions present in the cyanide electrolyte as compared to the nitrate electrolyte. The lower results obtained in using pure bismuth may be accounted for by heat being absorbed in the formation of the alloys, thus giving them a higher electromotive force.

III.

In the electrolyses which follow, the alloy to be refined was used as the anode of the electrolytic cell, while platinum foil formed the cathode upon which the silver was to be deposited. The platinum cathode was utilized in order that the silver deposit might be dissolved off for analysis, and, since the surface was very quickly coated with silver deposit, it acted practically the same as a silver sheet, such as would be used commercially.

On this series of tests the cyanide electrolyte was used. After a series of preliminary electrolyses had been made it was found

[7] E. B. Durham, Electrolytic Refining at the U. S. Mint, San Francisco, Cal.

TABLE I.—ALLOY "A"—CYANIDE ELECTROLYTE.

No. of Electrolysis 1	2	3	4	5	6	7	8	9	10	11
Weight of Deposit .....grams..0.0580	0.0559	0.1311	0.1616	0.1447	0.1017	0.1175	0.1798	0.1895	0.5041	0.2964
Surface of Cathode coated....sq. cm... 12	26	18	13	35	14.5	25	40	32	29	26
Average Current Strength....amperes..0.0075	0.0062	0.0116	0.0124	0.0123	0.0123	0.0144	0.0200	0.0156	0.0422	0.0238
Average N.D.$_{100}$ .....amperes..0.0625	0.0238	0.0645	0.0955	0.0352	0.0850	0.0576	0.0501	0.0488	0.1456	0.0916
Average Potential Difference....volts..1.50	1.75	1.87	1.90	1.96	2.01	2.10	2.40	2.50	2.60	2.70
Duration .....hours.. 4	4	5	4.5	4.5	3	3	4	4	4	4
Percent Silver in Deposit 99.5	100	99.8	99.9	99.6	99.6	100	99.4	100	99.2	...
Percent Bismuth in Deposit (by diff.).. 0.5	0	0.2	0.1	0.4	0.4	0	0.6	0	0.8	...
Deposit per Ampere-hour per 100 sq. cm. Cathode.....grams..0.232	0.588	0.407	0.377	0.916	0.359	0.681	0.898	0.972	0.865	0.810
KW-hours per Pound of Silver Deposited 0.353	0.352	0.375	0.298	0.340	0.331	0.350	0.484	0.373	0.394	0.393

No. of Electrolysis 12	13	14	15	16	17	18	19	20	21	22
Weight of Deposit .....grams..0.2453	0.3268	0.3735	0.4167	0.3464	0.3972	0.4862	0.4592	0.5359	0.5229	0.2293
Surface of Cathode coated....sq. cm... 46	54	29	26	63	29	27	67	66	23	42
Average Current Strength....amperes..0.0241	0.0299	0.0238	0.0321	0.0361	0.0328	0.0360	0.0357	0.0387	0.0335	0.0228
Average N.D.$_{100}$ .....amperes..0.0525	0.0555	0.0822	0.1233	0.0574	0.1123	0.1334	0.0533	0.0587	0.1456	0.0544
Average Potential Difference....volts..2.82	3.00	3.17	3.50	3.50	3.71	3.72	3.95	4.00	4.26	6.61
Duration .....hours.. 4	4	4	4	3	3	4	4	4	4	4
Percent Silver in Deposit 99.7	99.6	99.4	99.7	99.9	99.3	99.2	99.3	99.5	98.5	99.9
Percent Bismuth in Deposit (by diff.).. 0.3	0.4	0.6	0.3	0.1	0.7	0.8	0.7	0.5	1.5	0.1
Deposit per Ampere-hour per 100 sq. cm. Cathode.....grams..1.167	1.473	1.135	0.845	2.013	1.178	0.911	2.155	2.283	0.898	1.053
KW-hours per Pound of Silver Deposited 0.503	0.498	0.366	0.489	0.496	0.413	0.500	0.557	0.524	0.496	1.196

that polarization took place in the cell to such an extent that constant stirring would be necessary. Therefore during all the electrolyses the electrolyte was stirred by means of a glass rod bent at the end. At the upper end of the stirring rod was a

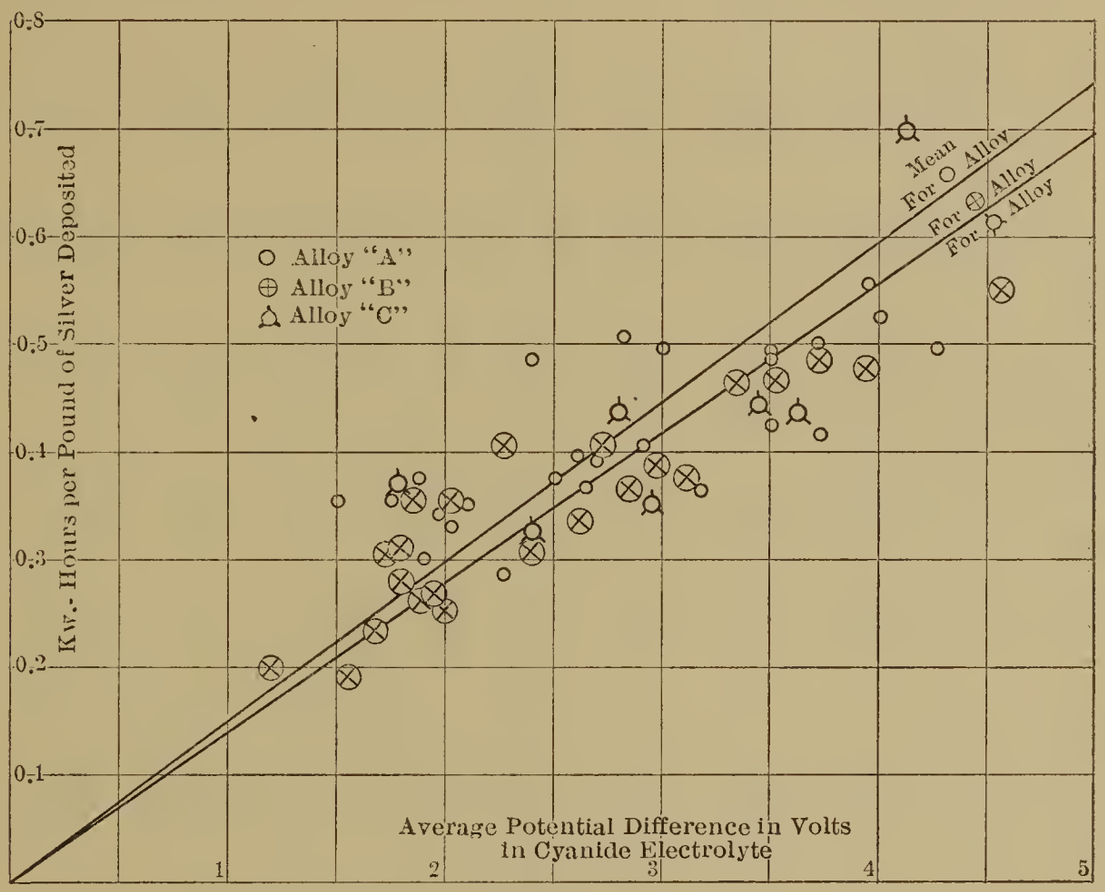

FIG. 1.

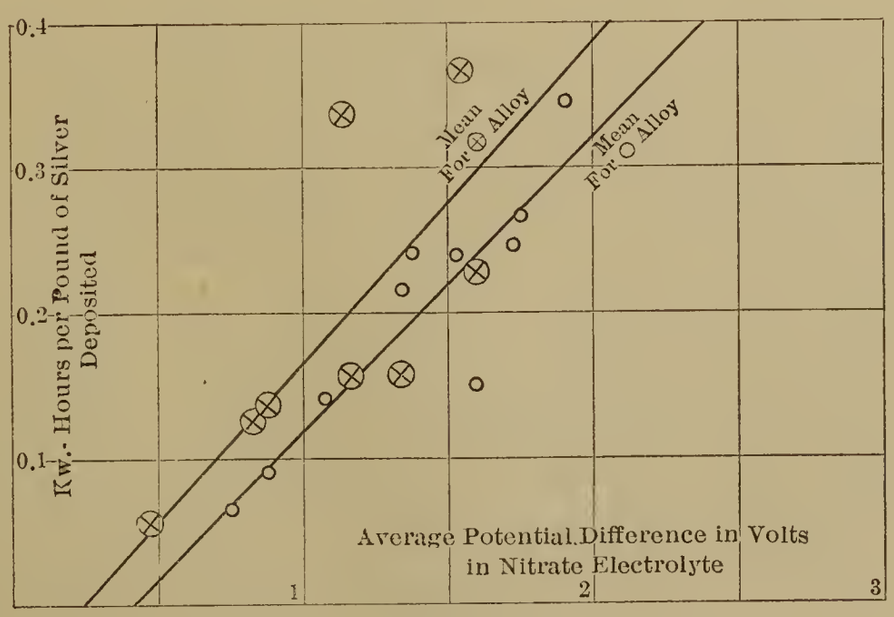

FIG. 2.

TABLE II.—ALLOY "B"—CYANIDE ELECTROLYTE.

No. of Electrolysis	23	24	25	26	27	28	29	30	31	32	33
Weight of Deposit .....grams..	0.2175	0.1679	0.2145	0.1748	0.1688	0.1579	0.4575	0.1654	0.1762	0.3462	0.3091
Surface of Cathode coated....sq. cm...	13	36	18	14	33	23	26	28	50	26	28
Average Current Strength....amperes..	0.0112	0.0110	0.0132	0.0133	0.0133	0.0121	0.0428	0.0160	0.0174	0.0246	0.0201
Average $N.D._{100}$ .....amperes..	0.0863	0.0306	0.0734	0.0951	0.0403	0.0527	0.1647	0.0572	0.0348	0.0947	0.0719
Average Potential Difference....volts..	1.67	1.71	1.80	1.80	1.85	1.95	2.00	2.02	2.26	2.61	2.72
Duration .....hours..	6	6	5.5	5	5.5	4	3	4	4	4	5
Percent Silver in Deposit	100	99.5	99.9	99.8	99.6	99.9	99.0	99.6	99.2	99.3	99.9
Percent Bismuth in Deposit (by diff.)..	0	0.5	0.1	0.2	0.4	0.1	1.0	0.4	0.8	0.7	0.1
Deposit per Ampere-hour per 100 sq. cm. Cathode.....grams..	0.421	0.916	0.533	0.368	0.763	0.750	0.926	0.725	1.266	0.915	0.861
KW-hours per Pound of Silver Deposited	0.234	0.307	0.276	0.310	0.357	0.269	0.255	0.354	0.405	0.337	0.402

No. of Electrolysis	34	35	36	37	38	39	40	41	42
Weight of Deposit .....grams..	0.5296	0.4884	0.4745	0.2397	0.5354	0.3513	0.6998	0.5819	0.6077
Surface of Cathode coated....sq. cm...	61	74	29	39	26	24	65	29	49
Average Current Strength....amperes..	0.0297	0.0350	0.0318	0.0184	0.0388	0.0255	0.0469	0.0410	0.0482
Average $N.D._{100}$ .....amperes..	0.0487	0.0473	0.1097	0.0472	0.1492	0.1062	0.0722	0.1413	0.0985
Average Potential Difference....volts..	2.86	2.96	3.11	3.34	3.52	3.71	3.93	4.59	6.69
Duration .....hours..	5	4	4	4	4	4	4	4	4
Percent Silver in Deposit	99.6	99.6	99.2	99.6	99.4	99.7	99.4	99.0	99.5
Percent Bismuth in Deposit (by diff.)..	0.4	0.4	0.8	0.4	0.6	0.3	0.6	1.0	0.5
Deposit per Ampere-hour per 100 sq. cm. Cathode.....grams..	2.178	2.580	1.080	1.271	0.898	0.827	2.422	1.029	1.541
KW-hours per Pound of Silver Deposited	0.364	0.385	0.378	0.465	0.463	0.489	0.478	0.550	0.961

small pulley, connected by a string belt to the pulley of a direct-current motor. The vessel used for the cell was a crystallizing dish 9 centimeters in diameter and 5 centimeters deep. Readings of the current strength and potential difference at the cell terminals were taken hourly, using Köhler milliammeters and Weston voltmeters.

Table I gives the results when "A" was used as anode.

Table II gives the results when "B" was used as anode.

Table III gives the results when "C" was used as anode.

In a large majority of cases the cathode deposit of silver was clean and white, but in a few cases, where the current density was relatively high, the deposit was brassy or iridescent. The deposit was fine-grained and quite adherent.

The anode residues from alloy "A" were dark brownish-gray and fine-grained. Those from alloy "B" were light gray and of a coarser structure. The anode residues from alloy "C" were intermediate in their characteristics, but resembled those from alloy "A" much more than the residues from alloy "B." In all cases a portion of these residues separated from the anode on account of the stirring.

The analyses of the alloys and deposits were made by determining the silver by Volhard's thiocyanate method[8] and calculating the bismuth by subtracting the weight of silver from the total weight.

IV.

In order to obtain data on the conditions after electrolysis has taken place for a longer time than in the electrolyses of Part III, eight electrolyses were carried on until the anode fell apart or the voltage began to increase unusually rapidly. In order to reach this condition within a reasonable time, smaller anodes were used. In these eight electrolyses the cathodes were of silver foil, but in other respects conditions were similar to those described in Part III. The cyanide electrolyte was used. The cyanide contents of the electrolytes were determined by precipitation as silver cyanide and the results then confirmed by igniting and weighing as silver.[9] Table IV gives the results of these electrolyses.

[8] Treadwell and Hall, Analytical Chem. II, 543.
[9] Treadwell and Hall, Analytical Chem. II, 259.

TABLE III.—ALLOY "C"—CYANIDE ELECTROLYTE.

No. of Electrolysis	43	44	45	46	47	48	49
Weight of Deposit ....grams..	0.0754	0.2662	0.3429	0.4248	0.5631	0.5130	0.2614
Surface of Cathode coated....sq. cm...	13	25	33	28	52	28	39
Average Current Strength....amperes..	0.0086	0.0198	0.0293	0.0278	0.0402	0.0340	0.0245
Average $N.D._{100}$ .....amperes..	0.0661	0.0792	0.0888	0.0993	0.0774	0.1213	0.0629
Average Potential Difference....volts..	1.78	2.40	2.80	2.95	3.43	3.61	4.11
Duration .....hours..	4	4	4	4	4	4	4
Percent Silver in Deposit	100	...	100	99.9	99.4	99.5	99.7
Percent Bismuth in Deposit (by diff.)..	0	...	0	0.1	0.6	0.5	0.3
Deposit per Ampere-hour per 100 sq. cm. Cathode.....grams..	0.285	0.841	0.965	1.069	1.817	1.057	1.039
KW-hours per Pound of Silver Deposited	0.368	0.324	0.434	0.350	0.444	0.434	0.698

TABLE IV.—CYANIDE ELECTROLYTE.

No. of Electrolysis	50	51	52	53	54	55	56	57
Weight of Deposit ....grams..	0.8992	3.4252	2.8971	2.1118	1.5098	2.3653	2.0073	0.6166
Surface of Cathode coated....sq. cm...	17	37	22	41	16.3	35	16	41.3
Average Current Strength....amperes..	0.0147	0.0474	0.0409	0.0291	0.0227	0.0451	0.0428	0.0107
Average $N.D._{100}$ .....amperes..	0.0865	0.1281	0.1859	0.0701	0.1392	0.1288	0.2659	0.0259
Average Potential Difference....volts..	2.26	2.90	3.49	2.64	1.56	1.88	2.41	1.20
Duration .....hours..	17	22	19	22	18	16	15	21
Percent of Silver in Deposit 99.2		98.1	98.8	98.2	99.2	99.5	99.8	99.3
Percent Bismuth in Deposit (by diff.)..	0.8	1.9	1.2	1.8	0.8	0.5	0.2	0.7
Percent of Anode-residue which fell off	13.4	28.3	24.8	20.2	82.4	28.5	20.2	79.8
Percent of (CN) Content of Electrolyte lost per hour	0.29	0.60	0.68	0.48	1.01	2.62	1.83	1.08
Deposit per Ampere-hour per 100 sq. cm. Cathode .....grams..	0.612	1.215	0.819	1.352	0.602	1.146	0.503	1.133
KW-hours per Pound of Silver Deposited	0.285	0.401	0.425	0.363	0.192	0.260	0.305	0.199

Alloy A was used as anode in Electrolyses 50, 51, 52, and 53.
Alloy B was used as anode in Electrolyses 54, 55, 56, and 57.

Logs of Electrolyses in Table IV.

Nos.	50		51		52		53		54		55		56		57	
Hours	Volts	Amp.	Volts	Amp	Volts	Amp.	Volts	Amp.	Volts	Amp.	Volts	Amp.	Volts	Amp.	Volts	Amp.
0	1.80	0.0175	2.60	0.0502	2.56	0.0459	1.89	0.0330	1.30	0.0232	1.42	0.0483	1.61	0.0453	1.15	0.0130
1	2.10	0.0160	2.62	0.0526	2.71	0.0459	2.36	0.0318	1.38	0.0236	1.47	0.0489	1.71	0.0452	1.13	0.0132
2	2.30	0.0144	2.69	0.0511	2.80	0.0454	2.49	0.0310	1.32	0.0236	1.49	0.0483	1.88	0.0450	1.17	0.0132
3	2.19	0.0151	2.69	0.0502	2.80	0.0448	2.45	0.0307	1.35	0.0236	1.50	0.0484	2.25	0.0424	1.20	0.0132
4	2.16	0.0152	2.71	0.0494	2.81	0.0450	2.49	0.0309	1.44	0.0234	1.62	0.0481	2.40	0.0416	1.20	0.0133
5	2.20	0.0150	2.73	0.0484	2.89	0.0446	2.49	0.0307	1.48	0.0230	1.60	0.0471	2.41	0.0408	1.20	0.0132
6	2.22	0.0151	2.75	0.0484	2.98	0.0445	2.49	0.0309	1.47	0.0230	1.65	0.0466	2.50	0.0402	1.19	0.0132
7	2.22	0.0143	2.73	0.0480	3.10	0.0425	2.51	0.0301	1.50	0.0229	1.70	0.0462	2.54	0.0398	1.20	0.0133
8	2.19	0.0146	2.70	0.0482	3.20	0.0435	2.57	0.0311	154	0.0224	1.75	0.0448	2.59	0.0391	1.19	0.0132
9	2.35	0.0144	2.70	0.0479	3.25	0.0429	2.60	0.0307	1.58	0.0223	1.79	0.0445	2.68	0.0387	1.20	0.0132
10	2.35	0.0139	2.76	0.0471	3.30	0.0422	2.60	0.0305	1.59	0.0220	1.80	0.0442	2.58	0.0390	1.18	0.0132
11	2.38	0.0135	2.82	0.0455	3.31	0.0415	2.60	0.0300	1.60	0.0221	1.88	0.0434	2.54	0.0397	1.20	0.0132
12	2.38	0.0136	2.82	0.0451	3.44	0.0409	2.66	0.0300	1.63	0.0221	2.05	0.0412	2.60	0.0399	1.20	0.0132
13	2.40	0.0137	2.87	0.0456	3.48	0.0409	2.65	0.0305	1.63	0.0222	2.08	0.0406	2.61	0.0391	1.18	0.0132
14	2.44	0.0137	2.88	0.0442	3.54	0.0407	2.65	0.0300	1.63	0.0224	2.08	0.0412	2.66	0.0393	1.20	0.0133
15	2.44	0.0136	2.91	0.0428	3.61	0.0392	2.70	0.0300	1.60	0.0222	2.05	0.0407	2.66	0.0392	1.20	0.0133
16	2.44	0.0135	3.00	0.0413	3.60	0.0393	2.76	0.0298	1.60	0.0220	2.14	0.0391	.....	.....	1.20	0.0133
17	2.43	0.0135	3.06	0.0390	3.97	0.0374	2.84	0.0296	1.68	0.0219	.....	.....	.....	.....	1.20	0.0132
18	.....	.....	3.10	0.0388	4.01	0.0365	2.74	0.0300	1.80	0.0213	.....	.....	.....	.....	1.20	0.0132
19	.....	.....	3.14	0.0404	5.00	0.0314	2.83	0.0303	.....	.....	.....	.....	.....	.....	1.20	0.0133
20	.....	.....	3.20	0.0398	.....	.....	2.86	0.0313	.....	.....	.....	.....	.....	.....	1.20	0.0132
21	.....	.....	3.24	0.0386	.....	.....	2.87	0.0315	.....	.....	.....	.....	.....	.....	1.20	0.0132
22	.....	.....	3.27	0.0377	.....	.....	2.87	0.0316	.....	.....	.....	.....	.....	.....	.....	.....
Aver.	2.26	0.0147	2.90	0.0474	3.49	0.0418	2.64	0.0316	1.56	0.0227	1.88	0.0451	2.41	0.0437	1.20	0.0132

TABLE V.—ALLOY "A"—NITRATE ELECTROLYTE.

No. of Electrolysis	58	59	60	61	62	63	64	65	66	67
Weight of Deposit ....grams.	0.2962	0.3322	0.4637	0.3997	0.5351	0.6084	0.4925	0.5254	0.3840	0.4549
Surface of Cathode coated....sq. cm.	20	75	70	23	63	46	29	65	26	22
Average Current Strength....amperes.	0.0143	0.0190	0.0444	0.0353	0.0517	0.0526	0.0337	0.0550	0.0441	0.0460
Average $N.D._{100}$ ....amperes.	0.0715	0.0257	0.0634	0.1535	0.0821	0.1143	0.1162	0.0846	0.1696	0.2090
Average Potential Difference....volts.	0.75	0.87	1.08	1.35	1.37	1.53	1.60	1.73	1.75	1.89
Duration ....hours.	4	4	4	4	4	4	3	3	3	4
Percent Silver in Deposit	90.0	92.7	90.9	92.4	91.4	94.8	96.3	93.6	93.6	93.7
Percent Bismuth in Deposit (by diff.).	10.0	7.3	9.1	7.6	8.6	5.2	3.7	6.4	6.4	6.3
Deposit per Ampere-hour per 100 sq. cm. Cathode....grams.	1.036	3.232	2.506	0.651	1.629	1.331	1.412	2.070	0.754	0.544
KW-hours per Pound of Silver Deposited	0.066	0.090	0.141	0.216	0.240	0.240	0.149	0.247	0.266	0.347

TABLE VI.—ALLOY "B"—NITRATE ELECTROLYTE.

No. of Electrolysis	68	69	70	71	72	73	74	75
Weight of Deposit ....grams.	0.2636	0.2446	0.2302	0.2187	0.2787	0.2925	0.2072	0.2522
Surface of Cathode coated....sq. cm.	70	27	26	26	70	65	28	29
Average Current Strength....amperes.	0.0166	0.0205	0.0198	0.0352	0.0209	0.0191	0.0269	0.0193
Average $N.D._{100}$ ....amperes.	0.0237	0.0760	0.0761	0.1354	0.0299	0.0294	0.0961	0.0666
Average Potential Difference....volts.	0.46	0.82	0.86	1.14	1.16	1.34	1.55	1.60
Duration ....hours.	4	4	4	4	4	4	4	4
Percent of Silver in Deposit	99.8	91.4	98.2	83.5	95.8	98.0	95.1	91.1
Percent Bismuth in Deposit (by diff.).	0.2	8.6	1.8	16.5	4.2	2.0	4.9	8.9
Deposit per Ampere-hour per 100 sq. cm. Cathode ....grams.	2.799	0.806	0.756	0.404	2.332	2.487	0.539	0.946
KW-hours per Pound of Silver Deposited	0.053	0.124	0.134	0.333	0.151	0.139	0.365	0.222

V.

Using the nitrate electrolyte, it was found that stirring was necessary, as in the case of the cyanide electrolyte. The cathode silver deposit was coarse-grained and not very adherent. The anode residues showed a strong tendency to slime off into the solution, and those from alloy "A" particularly were in quite small particles. To keep the anode residue separated from the cathode deposit the anodes were encased in fine lawn bags. In other respects the apparatus was the same as was used for the electrolysis with the cyanide electrolyte.

Table V gives the results when alloy "A" was the anode.

Table VI gives the results when alloy "B" was the anode.

In several cases the electrolyte became discolored by what may have been bismuth in colloidal suspension. If the particles were positively charged their wandering would be toward the cathode, and this would account for the relatively high percentage of bismuth in the deposit. There was not sufficient time to investigate this matter.

CONCLUSIONS.

(1) It is probable, from the present meagre electromotive force determinations. that silver-bismuth alloys are formed with an accompanying absorption of heat, giving them a higher electromotive force than pure bismuth.

(2) In the cyanide electrolyte.

(a) A deposit of silver containing less than 1 percent of bismuth may be obtained by using a current having a normal density for 100 sq. cm. of not more than 0.14 ampere. The current density gradually decreases during the electrolysis. All current density results are approximate, due to the uncertainty of cathode surface measurements.

(b) The potential difference between the electrodes gradually increases, through a small range, during the electrolysis, but may safely be as high as 6 volts.

(c) The required energy input is about 0.25 kw. hour per pound of silver deposited for a potential difference of 1.5 volts. This value is increased by 0.11 kw. hour per volt of increase in the potential difference.

(3) In the nitrate electrolyte.

(a) The silver deposits had comparatively high bismuth contents, even for low current densities. The results showed no great regularity.

(b) The potential difference between the electrodes must be kept down almost to the electromotive force of the cell in order to get a good separation.

(c) The required energy input, expressed in kw. hours per pound of silver deposited, is about 0.06 for a potential difference of 0.5 volt. There is an increase of 0.15 kw. hour for an increase of 1 volt in the potential difference.

(4) Comparison of the electrolytes.

(a) The nitrate electrolyte demands a weaker current, which calls for a much larger electrode surface for the same rate of deposit.

(b) The percentage of bismuth in the cathode deposits is more irregular and uncertain for the nitrate electrolyte, possibly due to colloidal conditions in the anode slimes.

(c) The necessary energy input increases more rapidly for higher voltages in the nitrate electrolyte than in the cyanide electrolyte.

(d) The deposit from the cyanide electrolyte is quite adherent, and the use of anode bags is avoided. The bismuth content of the deposit, using the cyanide electrolyte, is small enough to be gotten rid of in the melting, without occasioning a large loss.

ACKNOWLEDGMENT.

I am indebted to Professor G. H. Clevenger for suggesting the subject of this investigation, and to Professor S. W. Young, under whose direction the work has been carried out, for many valuable suggestions.

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MINERAL ELECTRODES.

By Roger C. Wells,

Introduction.

It is generally known that pyrolusite, magnetite, and pyrite are conductors of electricity but it does not seem to have been recognized that a number of other sulphides are even better conductors than pyrite and can consequently serve as electrodes. The object of this preliminary paper is to set forth some of the phenomena which have been discovered to occur when conducting minerals function as electrodes in aqueous solutions.

The minerals studied, in the approximate order of their conductivity, are galena, pyrrhotite, magnetite, chalcopyrite and pyrite. These substances are attackable in various degrees in the process of electrolysis, depending upon whether they function as cathode or anode. As voltaic electrodes some of them develop potentials which are comparable with those shown by the metals in contact with solutions of their salts.[1]

Electrolysis.

Sodium carbonate was electrolyzed for 5 hours with a current of 0.04 ampere, using electrodes of pyrites. As cathode, the pyrite remained bright and lost only 0.0025 g. Hydrogen was evolved. As anode the pyrite became coated with yellow hydroxide of iron, the gas evolved was less, after drying the electrode showed a loss of 0.0495 g. and sulphate was formed in the solution. It was attempted to oxidize the sulphur in a small quantity of finely ground pyrite in the bottom of a platinum dish

[1] Suggestions of these facts are found in the following papers: R. W. Fox. The Electro-Magnetic Properties of Metalliferous Veins in the Mines of Cornwall. Phil. Trans. 1830. Pt. 1, 399-414. W. Skey. On the Electromotive Power of Metallic Sulphides. Trans, and Proc. New Zealand Institute 3, 232-236 (1871). Carl Barus. The Electrical Activity of Ore Bodies, in "Geology of the Comstock Lode," by George F. Becker. U. S. Geological Survey, Monograph, 3, 309-367 (1882). V. H. Gottschalk and H. A. Buehler. Oxidation of Sulphides. Economic Geology, 7, 15-34 (1912).

by making it anode in a sodium carbonate solution, but the powder was not attacked as well as the large crystal had been. In nitric acid the behavior of pyrite as cathode and anode was similar although the cathode showed a slightly greater loss, 0.0098 g. to 0.0715 for the anode.

It is very easy to precipitate copper, iron or other metal upon cathodes of pyrite. If pyrite is made anode in copper sulphate solution black copper sulphide is formed and clings to the electrode. What is rather remarkable, pyrite remains almost unchanged in weight and lustre as anode in ferrous sulphate solution, which seems to be due to the electrolytic regeneration of the pyrite as fast as it is decomposed.

In sodium polysulphide solutions it is again chiefly the anode of pyrite which loses in weight.

TABLE I.

Single Potential of Electrode to N/1 KCl.

Pyrolusite	+0.93
Pyrite	0.90
Marcasite	0.72
Pyrrhotite	0.56
Magnetite	0.40
Galena	0.38
Commercial FeS	—0.03

Magnetite shows very little change in weight as cathode; as anode it gains slightly. As a matter of fact, magnetite has been employed commercially in large electrodes so it is superfluous to describe its behavior.

Galena as cathode suffers some mechanical disintegration along cleavage planes, but the chemical attack is slight. The anode becomes covered at first with lead sulphate and eventually with lead peroxide, with a marked gain in weight.

Anodes of graphite are said to be much more oxidizable in acid solutions than in alkaline solutions.

Electromotive Force Measurements.

The potentials shown by these electrodes against various solutions depend partly upon the specimen used, but to a much greater degree upon the nature of the solution. As a preliminary basis of reference they were measured against normal potassium

chloride solution, using a normal calomel electrode as the other half electrode. Since the potentials after the specimens are treated with acids or alkalies do not immediately return to their initial value the best values would seem to be those shown by fresh specimens. A list of values obtained from fresh specimens is given in Table I. The measurements were made by the usual compensation method of Poggendorff with Lippmann electrometer as indicating instrument. The single potentials were computed by adding (or subtracting) the value .56 volt from the total measured voltage.

TABLE II.

Variations of Potential with Time, N/1 KCl.

	1	2	3	4
April 11.....	1.01	0.96	0.94	0.72
May 4.....	0.99	0.92	0.88	0.71
June 14.....	0.93	0.88	0.87	0.68
" 18.....	0.94	0.88	0.85	0.83
" 25.....	0.97	1.00	0.83	0.56

1. Pyrite collected by A. A. Julien (No. 39).
2. Pyrite from Elba.
3. Octahedron of Pyrite, French Creek, Penn.
4. Marcasite, coxcomb, collected in Missouri by C. E. Siebenthal.

Chalcopyrite and chalcocite fall between marcasite and galena. The above order is consistent with the fact that marcasite is more easily oxidized than pyrite.

Most specimens of pyrite gave potentials ranging from 1.01 to 0.76, although one specimen went as low as 0.56. Marcasite showed values from 0.56 to 0.83. This difference would therefore appear to be a quick means of distinguishing pyrite from marcasite. A nodule found at a depth of 7 feet gave 0.87 and was therefore mostly pyrite. The variations of several of these specimens from day to day (out of the solution) is shown in Table II.

A change in the electrolyte affects the potential of these electrodes markedly, especially a change in the acidity or alkalinity of the solutions.

Pyrite and marcasite are most positive in acid solutions. Their potentials fall as the solutions become alkaline and they may even become negative in alkaline sulphide solutions. For example a certain specimen of pyrite gave +0.95 volt in N/1 H_2SO_4, 0.80 in N/1 KCl, 0.14 in N/1 NaOH and —0.17 in N/1 Na_2S.

Galena, similarly, gave 0.32 in N/1 H_2SO_4, 0.28 in N/1 KCl, 0.11 in N/1 NaOH, and —0.19 in N/1 Na_2S.

Fresh chips of magnetite gave about +0.40 volt against N/1 KCl, 0.94 in N/1 H_2SO_4 and —0.22 in N/1 NaOH.

In alkaline sulphide solutions the potentials are far more constant and reproducible than in acids or salt solutions, but there is not as much difference between the values for the different sulphides. Moreover there is very little difference between values shown by Na_2S and $Na_2S_{4.5}$. Thus in N/1 Na_2S galena gave —0.19, pyrite —0.17, artificial FeS —0.17, pyrrhotite —0.09 and marcasite —0.07. In N/1 $Na_2S_{4.5}$ galena and pyrite gave —0.16 and marcasite —0.07. The same specimen of pyrite after washing with water gave +0.36 in N/1 KCl, after dipping in acid, cleansing, and replacing in N/1 KCl, +0.74, and finally when replaced in Na_2S — 0.17, the previous value. It may be that these potentials in alkaline sulphide solution represent fewer phases, as for example pyrite and FeS and no others. The values in Na_2S are evidently more reproducible than those in KCl.

Theory.

From facts so far obtained it seems difficult to characterize these electrodes. At first thought one might decide to class them in the group of metallic electrodes having a very insoluble depolarizer, but the direction and value of their electromotive forces do not correspond to that view. In most solutions the electrodes are positive, tending to react chemically with positive ions to form oxides or sulphides while the positive charge passes from the ion to the electrode, thus constituting the current over the wire to the other electrode. It would accordingly be appropriate to term them *reducing* or *sulphidizing* electrodes. On the other hand, the great effect of alkalinity or acidity upon their potentials suggests that they may function in part as oxygen (or hydrogen) electrodes and it seems reasonable to con-

clude that the high potential of oxygen might interfere with the lower potential of sulphur even when sulphur was present in excess. Finally in alkaline sulphide solutions the electrodes become negative, the tendency is for sulphide ions to discharge and the electrode becomes an *oxidizing* one.

It appears strange to class sulphides with oxidizing substances, but that is where they fall for the most part according to the potential criterion; on the other hand the nature of the solution evidently determines the classification, since in alkaline sulphide solutions they are negative and hence become reducing electrodes. In short these minerals behave as unattackable conductors and derive their potentials from the solutions.

With oxides one can reasonably hope to obtain reversible electrodes because the intermediate substance, water, does not escape. With sulphides the chief conditions of reversibility would appear to be to maintain a supply of sulphide either as alkaline sulphide or as an insoluble metallic sulphide. These matters will require much further experimental work for their complete elucidation.

In electrolysis these minerals may also function in some degree as unattackable electrodes. Evidently the time factor here does not permit equilibrium conditions to be rapidly obtained so that hydrogen or oxygen is evolved more easily than the electrode is decomposed. As has been pointed out, a moderate current evolves chiefly hydrogen from a pyrite cathode, whereas the equilibrium probably corresponds to the formation of a sulphide.

The sulphides of low potential convert ionized hydrogen into hydrogen sulphide spontaneously, galena barely gives a test for hydrogen sulphide with dilute acids, while marcasite and especially pyrite are very stable in acids. The explanation of these facts is not obvious, for the differences in simple solubility are not great.

The electromotive forces under discussion are probably the cause of such earth currents as have been noted in mines. Moreover, surface solutions are usually acidic, deep solutions neutral or alkaline, which would cause currents in veins to flow upward through the solutions and downward through mineral deposits,

corresponding with the observation made by Fox in the mines of Cornwall. Whenever single crystals of pyrite are bathed by a solution of gold, a metal of low electro-affinity, local electrical action must tend to cause the deposition of the gold. This may be one reason for the frequent association of gold and pyrite.

Pyrite in contact with acid solutions must protect itself from oxidation by its own electrical polarization (or by a film of hydrogen) and the other sulphides must act similarly though in smaller degree, so that with two sulphides in contact the one of lower potential will act as anode to the other and hence, as has been pointed out, undergo oxidation first. The fact of this increased oxidation of one sulphide in contact with another was noted in chemical studies by Gottschalk and Buehler before they developed an explanation in terms of electrical action.

Washington, D. C.

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THE VAPOR PRESSURE OF ZINC AMALGAMS.

By Joel H. Hildebrand,

Among the greatest triumphs of modern science must be reckoned the discovery and application of the laws governing dilute solutions, which may be grouped under the general idea of the application to solutions of the Rule of Avogadro. In all the development of chemistry there have probably been no principles which have proved to be such valuable instruments in the hands of investigators. However, the increasing deviations from these laws shown as solutions approach ordinary concentrations have produced the conviction that Avogadro's Rule as applied to solutions must be regarded as an extrapolation, and that a more exact law, applicable to concentrated solutions, must be established. The Law of Raoult for the lowering of vapor pressure, announced from a purely empirical basis, has more recently received the theoretical foundation and experimental proof which indicate that it is probably the nearest approach that we possess to an exact law of a perfect solution.

The problem has been clearly stated and its solution indicated by Nernst where he states,[1] "wir dürfen die aktive Masse des Lösungsmittels proportional der Koncentration des von ihm entsandten Dampfes setzen . . . Dies Resultat wäre durch kinetische Betrachtungen nicht zu erhalten gewesen und ist auch erst von mir auf diesem Wege gefunden worden. Die Thermodynamik vermag uns also hierin weiter zu führen, und es sei betont, dass bei der Behandlung konzentrierter Reaktionsgemische sie allein gegenwärtig die theoretische Führung zu übernehmen im Stande ist; wären wir im Besitze von Regeln über die Dampfdrucke beliebig konzentrierter Gemische, so würden wir die Reaktionen solcher Systeme mit der gleichen Vollständigkeit

[1] Theoretische Chemie, 5th ed., p. 647.

behandeln können wie diejenigen verdünnter Lösungen." The vapor pressure of one component of a mixture is thus the direct measure of the "active mass" of the component in the mixture. The experimental advantage of referring active mass to vapor pressure rather than to osmotic pressure, for example, is obvious.

Now, the other side of the equation involves the expression of active mass in terms of the quantities of material present. This seems possible by following the suggestion originally made by Gibbs, and advocated since by Plank, van Laar and others, that the active mass of a component of a phase is proportional to its mol-fraction, *i. e.*, to the number of mols of the component divided by the total number of mols present. Combining this with the above expression of Nernst, we have the law that *the vapor pressure of a component of a mixture is proportional to its mol-fraction.* The constant of proportionality is given by making the mol-fraction 1, which shows it to be the vapor pressure of the substance in the pure state, that is, of the saturated vapor. The value of this law has been emphasized by a number of authors recently, among whom may be mentioned Dolezalek,[2] Lewis,[3] Möller,[4] and Washburn.[5] The interesting results of Dolezalek in determining the constitution of liquid mixtures and the importance of a reliable method of investigating the various problems of association, dissociation, and solvation, make, as Washburn says, the gathering of data along this line of great importance.

This study of the vapor pressure of amalgams was begun with the double purpose of testing the vapor pressure law upon solutions differing widely in physical nature from the organic mixtures to which it has hitherto been applied, and also of attacking the general problem of metal compounds from a new standpoint.

While the compounds of the metals with one another have been largely investigated in recent years by thermal analysis, the results so obtained allow nothing but inference concerning the nature of the liquid phase. The well-defined and varying physical constants of the metals promise much of interest as a result of a thorough study of their solutions in one another.

[2] Zeit, phys. Chem., **64**, 727 (1908); **71**, 191 (1910).
[3] Journ. Amer. Chem. Soc., **30**, 668 (1908).
[4] Zeit. phys. Chem., **65**, 226 (1909).
[5] Journ. Amer. Chem. Soc., **32**, 653 (1910).

The natural starting point of such a series of investigations is the amalgams, since they are liquid at not too extreme temperatures, and have measurable vapor pressures, allowing, therefore, their investigation by means of the vapor pressure law. The published work in this direction is very limited. The existence of hydrargyrates in solution has been the subject mainly of speculation.[6] The vapor pressures of very dilute amalgams have been studied in the comprehensive work published by Ramsay[7] a number of years ago, but the molecular weight of the metals was the object in view, and no conclusions were drawn regarding possible solvation, although such is clearly indicated in several cases.

In the light of what has been said it is evident that a further study of this problem using more concentrated solutions is of considerable importance. The results upon zinc amalgams here presented are the first of a series which the writer hopes to carry out.

Experimental Part.

1. Materials Used.—The mercury used was first washed in the apparatus described by the writer,[8] and then distilled as prescribed by Hulett.[9] The zinc was "Baker's Analyzed," the analysis giving 0.05 percent of lead, 0.004 percent of iron, no arsenic, and a trace of cadmium. An analysis made to confirm these figures gave 0.04 percent lead and 0.001 percent of iron. These amounts were far too small to influence the results.

2. Apparatus.—For the purpose of measuring the vapor pressure the amalgams were confined in tubes such as shown in Fig. 1. The internal diameter of this tubing was about 7 mm., thus minimizing the effect of the surface tension of the amalgam. In the first experiments the part between *b* and *c* was lacking. The part from *a* around to *b* was blown separately and fused onto the upper part after putting into it a weighed piece of zinc, which had previously been moulded into thin sticks and scraped free from surface oxide. The tube containing the zinc was then exhausted and enough mercury admitted carefully from a

[6] See Berthelot, Ann. Chim. phys. 5, **18**, 433. Haber, Zeit. anorg. Chem., **44**, 399 (1902); G. MacP. Smith, Zeit., anorg. Chem., **58**, 381 (1908).

[7] Journ. Chem. Soc., **55**, 521 (1889).

[8] Journ. Amer. Chem., **31**, 933 (1909).

[9] Phys. Rev., **33**, 307 (1911).

supply poured in beyond the stopcock to furnish an amalgam sufficient to fill the closed limb of the U-tube and extend well around the bend. The quantity of mercury used was determined after the experiment by cutting at *a*, and weighing the U-tube with and without amalgam. The amount of zinc being known,

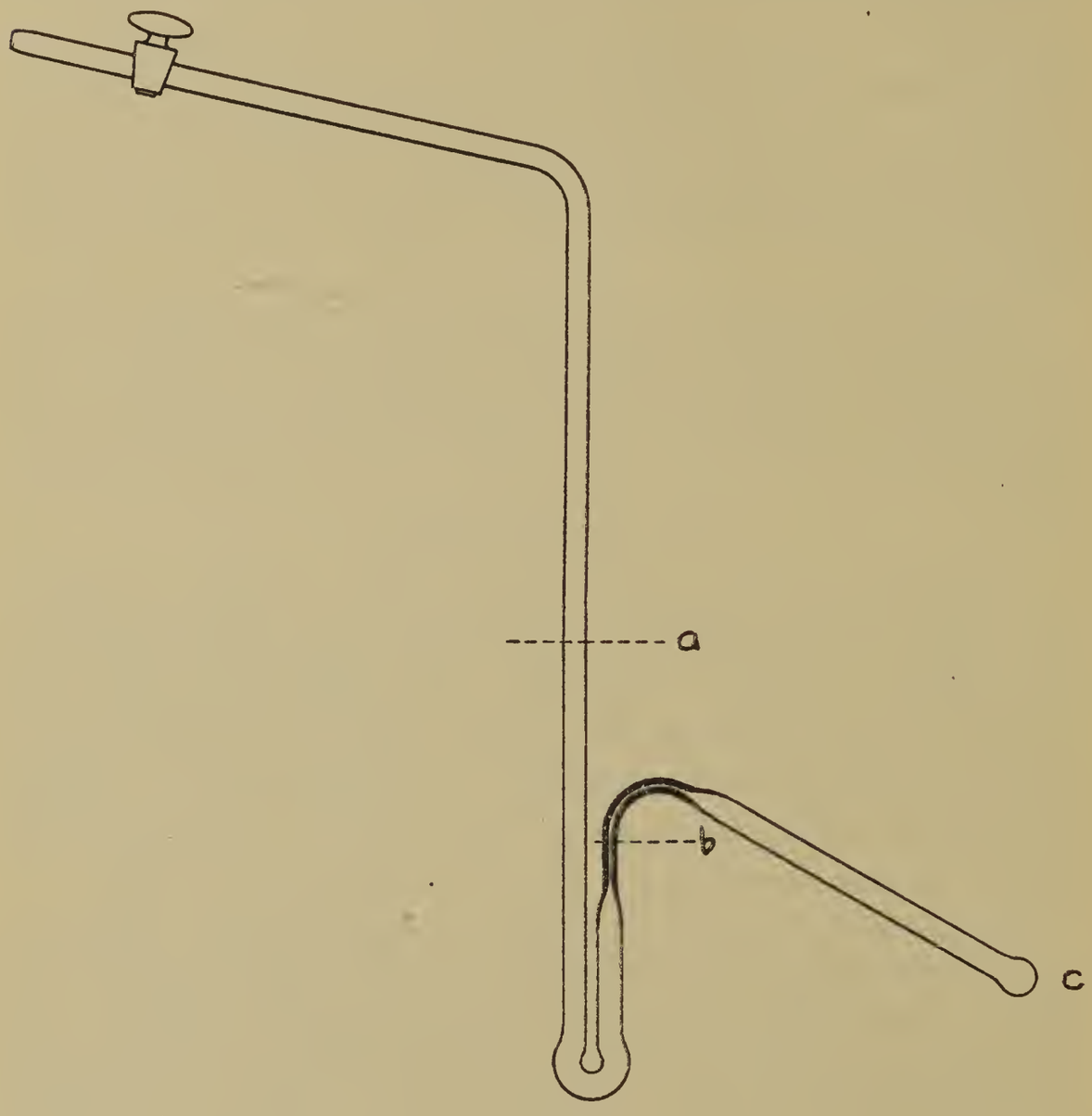

FIG. 1.

the mercury was given by difference. Vacuum reductions were not made, as the corrections thus made would have been beyond the limits of accuracy otherwise attainable. The tube now containing the mercury and zinc was heated while still exhausted, whereby the zinc amalgamated with the mercury and at the same time the short limb was boiled free from residual gas. The tubes were drawn to a point at *b* so that a minute bubble of gas could

be easily seen. In the later experiments with more concentrated amalgams, Nos. 29 to 32, it was found necessary, in order to avoid the presence of oxide, to fill the tubes in a different manner. The tube was blown as shown in the figure except that it was left open at *c*. After introducing the weighed zinc, at *c*, it was sealed at this point, the mercury introduced in a weighed amount at the other end, whereupon the tube was exhausted, filled with hydrogen and again exhausted. The mercury was then run into *b*-*c*, and hydrogen admitted to a pressure of slightly less than one atmosphere. On heating, the zinc amalgamated with the mercury and the amalgam was run through the capillary into the U, leaving behind the small amounts of oxide which had collected on the surface. The capillary was sealed at *b*, leaving the tube ready for insertion into the thermostat. A similar tube containing mercury alone, and filled, of course, without the above precautions, served to give the vapor pressure of mercury for comparison.

The measurements were carried out at 300° in a thermostat shown in Fig. 2, and constructed for the writer by the Caloris Company of Philadelphia. It was constructed on the plan of a vacuum bottle, the outer bottle was elongated so as to contain the heating liquid, diphenylamine, whose vapors heated the liquid in the inner bottle. This latter was ordinary commercial "Cottolene." The side tube shown in the figure served as an air-condenser for the vapors of diphenylamine not condensed in the lower parts of the apparatus. The cottolene, protected from the air as much as possible by asbestos coverings, stood the high temperature fairly well. It gave off endurable quantities of acrolein and had to be replaced after two days' use on account of darkening. The apparatus was protected on the outside by a cylinder of glass cut from a tall beaker, and the space between the top of this cylinder and the bottle was closed by a roll of asbestos paper. The cottolene was stirred vigorously by a stirrer, as shown, run at a high speed by an electric motor. The temperature was determined by means of a copper-constantin thermocouple, the cold junction of which was kept in ice in a vacuum bottle. The e.m.f. of the couple was read on a Siemens-Halske galvanometer. The temperatures given later are, however, taken

from the vapor pressure of the mercury as given by the careful measurements of Smith and Menzies.[10]

The vapor pressure of the mercury and amalgams at this temperature tends to make the liquid fall in the closed limb of

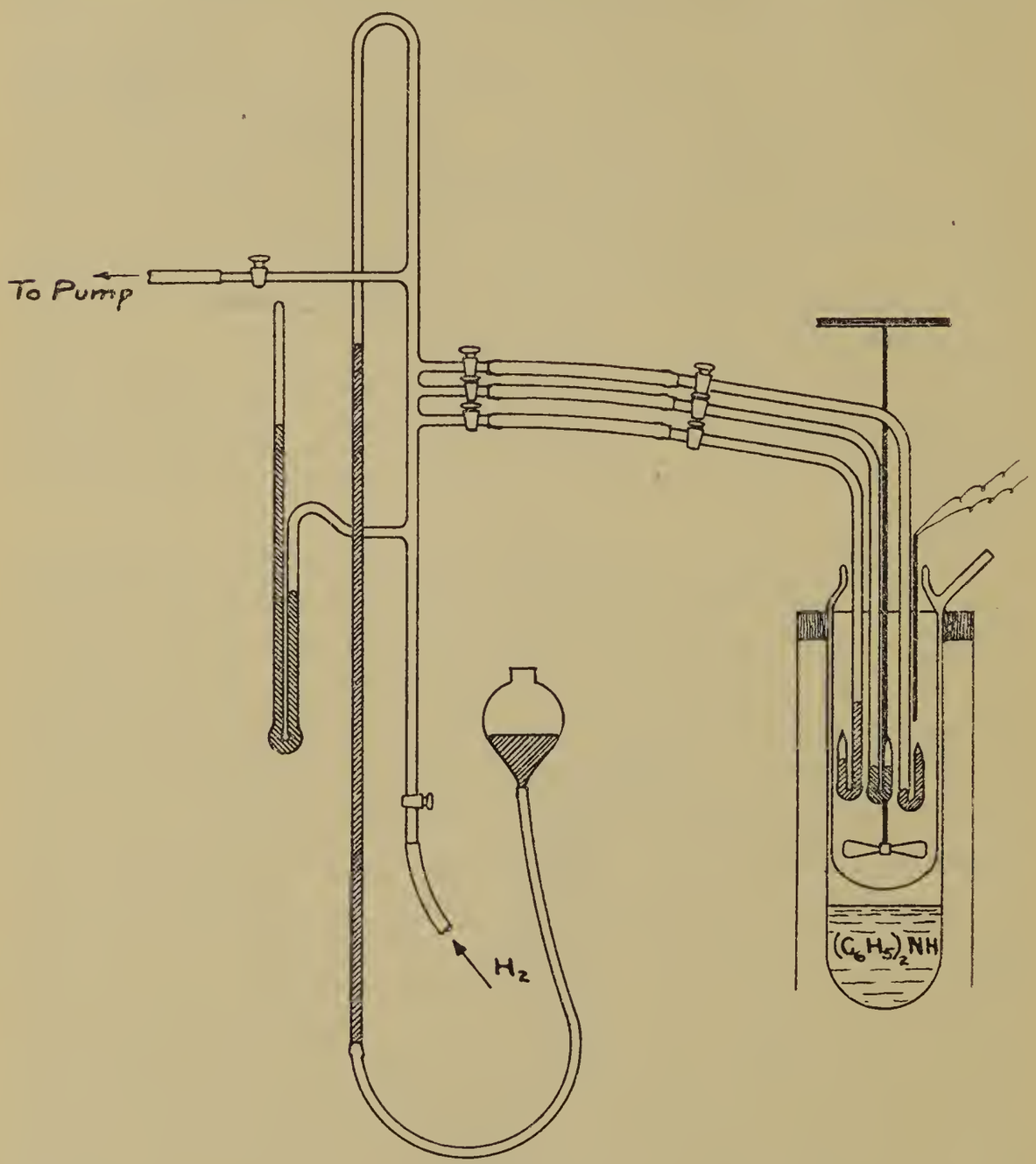

FIG. 2.

the U-tubes, and this was balanced and measured with the aid of the connections shown in the left of Fig. 2. The tube containing the mercury and two containing amalgam were connected as illustrated, and the apparatus, including the rubber connections, pumped free from air. The cocks of the U-tubes were then

[10] Journ. Amer. Chem. Soc., 22, 1434 (1910).

opened and hydrogen, from a Kipp generator, purified by passing over a heated copper spiral and drying with sulphuric acid, was admitted to a pressure sufficient, as the temperature of the thermostat rose to 300°, to keep the level of the amalgam in both limbs of one of the tubes approximately the same. Finer adjustment of pressure was made by means of the reservoir of mercury shown in the figure. This method of adjusting pressure seems easier than that used by Smith and Menzies.

The pressure adjusted so that the mercury stood at the same level in one of the tubes, the greater pressure in the closed limb of the tube containing the pure mercury forced the mercury to rise in the other limb to an amount equal to the difference in pressure of the amalgam and of mercury. This difference in level was read by means of a cathetometer, simultaneous readings being taken on the manometer giving the pressure of the amalgam direct. A number of readings were taken with each tube, the pressure being readjusted before each reading. The pressure was also frequently increased to make sure of the absence of gas in the closed limbs. All readings were reduced to mm. of mercury at 0°. The readings on the cathetometer, being in mm. at 300°, were reduced by the factor 0.947, which is the ratio of the density of mercury at 300°, 12.881, to that at 0°, 13.596.

TABLE I.

Expr. No. 31. Wt.Zn = 6.712; Wt.Hg = 12.230.

P	P_0	P/P_0	Temp.
111.9	241.8	0.463	299.4
108.9	240.8	0.453	299.0
112.4	241.3	0.466	299.1
111.9	241.3	0.464	299.1
108.9	237.8	0.458	298.5
109.9	238.8	0.460	298.7
110.9	240.8	0.461	299.0
111.9	241.3	0.463	299.1
112.9	242.1	0.466	299.5
		Mean 0.462	

In experiments 29-32, the difference in pressure had become too great for the dimensions of the thermostat, also the mercury showed a tendency to boil in the open limb, so that a second apparatus similar to that shown on the right of the figure was

used in connection with the U-tube of mercury. The mercury in this tube was now also adjusted to the same level and the pressure read independently on the attached manometer. The extra connections and the use of hydrogen were dispensed with in this part of the apparatus. This arrangement proved more satisfactory than the former where a cathetometer had to be used, and will doubtless be retained in future investigations.

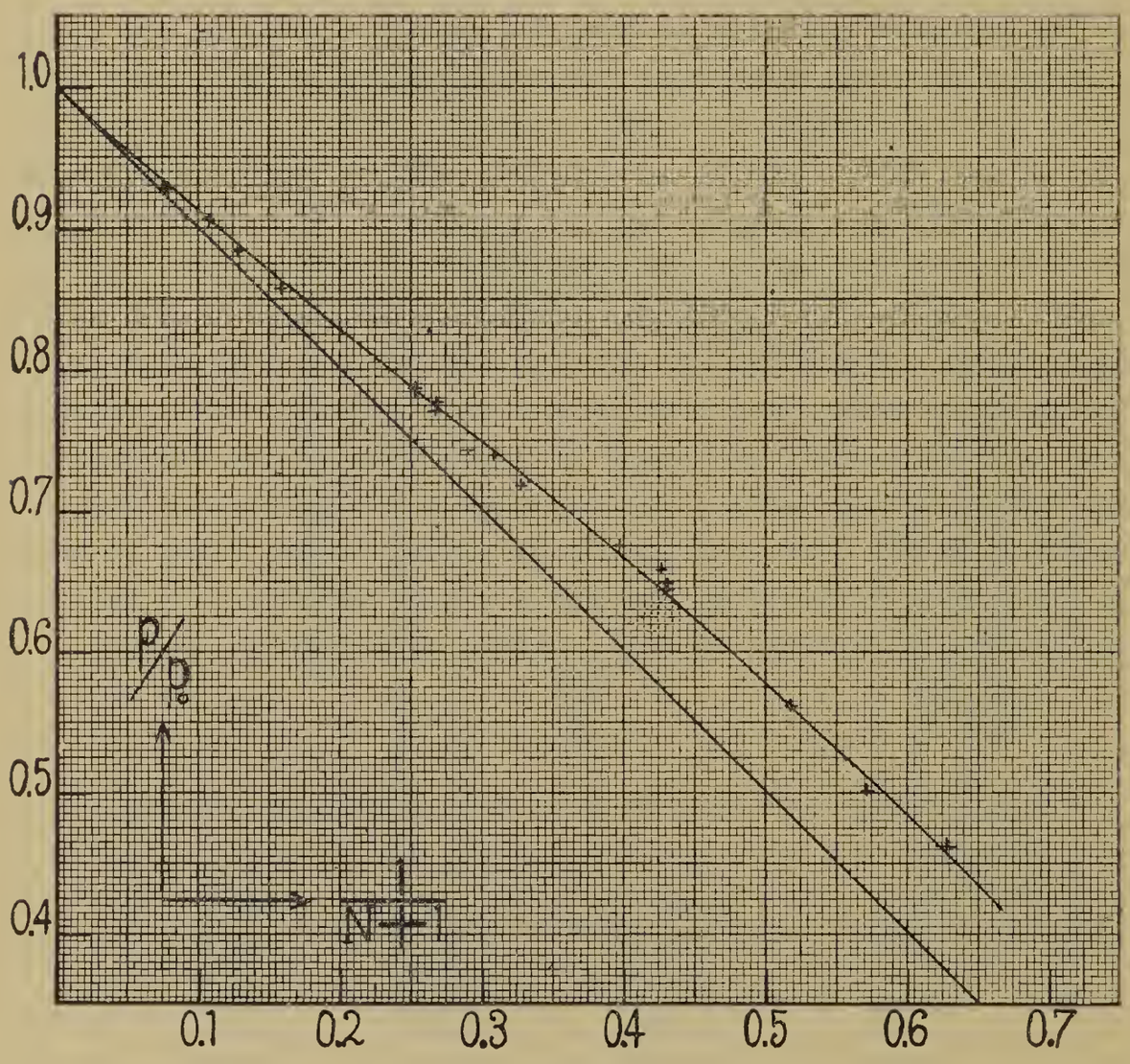

FIG. 3.

3. Results.—Table I gives a typical experiment, No. 31. In this, P_0 denotes the vapor pressure of mercury; P, that of the amalgam; N, the number of mols of mercury per mol of zinc. It will be seen that the slight changes in temperature affect the pressures in the same ratio, so that the simultaneous determination of the pressures made it useless to seek greater constancy in temperature.

Table II gives a summary of all the data secured, each line representing results similar to those of Table I. The values of the relative pressures, P/P_0, are plotted in the curve, Fig. 3, against the atom-percent of zinc, $N/N+1$, given in the fifth column of the table. If the amalgams were perfect solutions and obeyed the law $P/P_0 = N/N+1$, then the graph should be a straight line, and the values in the sixth and seventh columns of the table should agree. It will be seen that the pressures are considerably higher than they should be for a simple solution.

TABLE II.

No. of Expr.	No. of Observ.	Percent Zn	N	$\frac{1}{N+1}$	$\frac{N}{N+1}$	$\frac{p}{p_0}$	$\frac{N}{N+1-a}$	Δ
21	6	2.655	11.98	0.077	0.923	0.928	0.930	—0.002
8	9	3.72	8.461	0.107	0.893	0.906	0.906	+0.000
22	5	4.61	6.776	0.129	0.871	0.884	0.887	—0.003
6	10	5.74	5.353	0.158	0.842	0.854	0.863	—0.009
19	7	10.00	2.946	0.254	0.746	0.787	0.786	+0.001
12	6	10.63	2.747	0.267	0.733	0.771	0.774	—0.003
17	6	10.66	2.745	0.268	0.732	0.778	0.773	+0.005
20	5	11.75	2.458	0.290	0.710	0.743	0.756	—0.013
24	5	12.76	2.238	0.309	0.691	0.735	0.739	—0.004
18	4	13.74	2.056	0.328	0.672	0.718	0.725	—0.007
32	7	17.78	1.510	0.398	0.601	0.675	0.665	+0.010
25	8	19.52	1.348	0.426	0.574	0.658	0.642	+0.016
28	3	19.70	1.332	0.429	0.571	0.644	0.638	+0.006
26	6	19.80	1.325	0.431	0.569	0.649	0.636	+0.013
30	5	26.00	0.929	0.519	0.481	0.561	0.559	+0.002
29	8	30.42	0.747	0.572	0.428	0.501	0.501	—0.006
31	9	35.45	0.595	0.627	0.373	0.462	0.454	+0.008

How can these deviations be accounted for? This was done by assuming, as Dolezalek has done, that the solute is associated to some extent, and hence the number of mols of zinc is less than is assumed in the simple formula.

Suppose that the atomic mols of zinc unite partially according to the equation,

$$2Zn = Zn_2.$$

If a represents the number of mols of Zn_2 formed from 1 mol of Zn, there would remain $1 - 2a$ mols of Zn, and the total

number of mols present in the mixture would be $N + 1 - \alpha$. Applying the law of mass-action, using mol-fractions instead of concentrations, we obtain the equation:

$$\left(\frac{1 - 2\alpha}{N + 1 - \alpha}\right)^2 = K \frac{\alpha}{N + 1 - \alpha}$$

Solving this equation for α, we get

$$\alpha = 0.5 + \frac{KN - \sqrt{(KN + K)^2 + 4K(2N + 1)}}{2(K + 4)}$$

(The minus sign before the radical is evidently correct.) Now, since the relative pressure should be equal to the mol-fraction of mercury:

$$\frac{P}{P_0} = \frac{N}{N + 1 - \alpha}$$

Substituting the above value of α in this equation we obtain:

$$\frac{P}{P_0} = \frac{2N(K + 4)}{N(K + 8) + K + 4 + \sqrt{(KN + K)^2 + 4K(2N + 1)}}$$

The values given in the eighth column of Table II and represented by the curve in Fig. 3 were obtained by putting

$$K = 0.50,$$

when the equation becomes:

$$\frac{P}{P_0} = \frac{9N}{8.5N + 4.5 + \sqrt{0.25N^2 + 4.5N + 2.25}}$$

The last column, Δ, in the table gives the differences between the observed values of P/P_0 and $N/N + 1 - \alpha$, calculated by this equation. The closeness with which the results agree is very striking, admits of hardly any other conclusion than that the assumptions involved are correct. If zinc is associated in solution in mercury, then the vapor pressure law expresses the behavior of the solution up practically to the limit of the solubility of zinc in mercury at this temperature.[11]

[11] 70.5 atom percent zinc, according to Puschin, Zeit. anorg. Chem., 36, 201 (1903).

It is interesting, furthermore, to note the extent of the association at various concentrations, calculated from the value of $K = 0.5$.

N	100	10	1	0
Percent association	4	22	52	66.7

If zinc could exist in the liquid state at 300° it would accordingly be ⅔ associated to Zn^2.

University of Pennsylvania,
Philadelphia.

DISCUSSION.

Dr. G. S. Forbes: Dr. Hildebrand's assumption that the zinc in the zinc amalgam is partially polymerized is substantiated by a line of evidence which was obtained by Professor T. W. Richards and myself about 1904 in working on the potential of concentration cells of zinc amalgam. We investigated carefully the electromotive force of a number of these cells, and we found that in every case the result came out lower than that which would be calculated from the formula:

$$\pi = \frac{RT}{2F} ln \frac{c_1}{c_2} + \frac{\sqcup\!\sqcup}{2F}.$$

Here $\sqcup\!\sqcup$ is the positive heat of dilution. In this case the dilution heat of the zinc amalgam was absorbed. Now we got a very careful calorimetric measurement of the heat that was absorbed in the process. We found that it was by no means large enough to account for the discrepancy between the observed potential and the calculated potential, and we made the only assumption that could be made under these circumstances, in view of researches we had done on cadmium amalgams, that the zinc was partially polymerized, and that this caused the low value of the electromotive force. Now Ramsay, in a research to determine the state of metals in amalgams, had found that in general metals appear to be monatomic when dissolved in mer-

cury; although his results were rather crude, it appeared indisputably that all the values of $d\ p$ for zinc amalgams were too low. That is, it appeared that the zinc was polymerized at these higher temperatures, as well as lower temperatures. So these two lines of evidence are, I think, very much in favor of Dr. Hildebrand's main assumption.

Prof. E. W. Washburn: I will first say a word about the equation, $p = p_0 x$, in which p is the partial vapor pressure of any molecular species above a solution in which its mol-fraction is x, p_0 being an integration constant which is obviously equal to p for $x = 1$. In employing this equation to detect and measure association, or complex formation in solution, we must be very cautious, for it must be remembered that there are many cases for which the equation cannot hold and its failure in these instances cannot be explained by any assumptions as to molecular weight, complex formation or association. The equation simply does not hold for these cases, as the following considerations will show: (cf. Jour. Amer. Chem. Soc., **32**, 670 (1910).

Suppose that we have a system composed of two liquid phases which are not completely miscible. We will start by assuming that both phases are ideal solutions, that is, the partial vapor pressure of each molecular species from each phase is expressed by the above equation. Suppose that there are n different molecular species in our system. We will designate these different molecular species by $a, b, c, \ldots\ldots n$. On the above assumption of the validity of the vapor pressure law we will have for the vapor pressure of the molecular species a, from the first liquid phase

$$p_a = p_{oa} x_a$$

and from the second liquid phase, $p'_a = p_{oa} x'_a$.

Now by the Second Law of thermodynamics, $p_a = p'_a$ and hence x_a must equal x'_a. In other words, the molecular species a must have the same mol-fraction in both phases. In exactly the same way we can prove that each of the other molecular species must have the same mol-fraction in both phases. But if every molecular species in our system has the same mol-fraction in both phases the two phases are identical in composition, which cannot be the case if they are non-miscible.

Hence we must conclude that in a system composed of two solutions which are not completely miscible, the above vapor pressure law cannot hold, and its failure is a real one and not simply an apparent one to be explained away by some assumption as to association or complex formation. It is, therefore, a necessary—but not sufficient—condition that two liquids must be miscible in all proportions if they are capable of forming an ideal solution with each other.

What further condition is necessary? If we shake together two liquids like benzene and mercury, we all know that they separate into two phases, one phase composed of almost pure mercury and the other of almost pure benzene. The two liquids are so unlike that they will not mix. The molecules of the benzene cannot find congenial surroundings in the mercury nor the molecules of mercury in the benzene. If we substitute water for mercury we get a greater degree of miscibility. That is, the substance water is not so unlike benzene as is mercury. If we use alcohol in place of water, we have miscibility in all proportions. This complete miscibility, however, occurs only under protest, as evidenced by the heat effects and volume changes which accompany it. The two liquids *will mix* but only after some readjustment which in this particular case probably consists largely of an association of the alcohol molecules to form molecules of the formula $(C_2H_6O)_n$. If finally we use toluene in place of alcohol, the toluene molecules are so much like those of benzene that miscibility in all proportions takes place, easily, with practically no heat effects or volume changes. That is, a toluene molecule (or a benzene molecule) finds itself in practically the same "condition" whether it be surrounded entirely by toluene molecules, entirely by benzene molecules or by mixtures of the two in any proportions. This "condition" may be called the *thermodynamic environment* of the molecule. Whenever the thermodynamic environment of a molecular species in a solution is independent of its mol-fraction, the solution is an ideal solution; that is, the vapor pressure law, $p = p_0 x$, will always hold. When this condition is not fulfilled there will be deviations from this law and these deviations are not merely apparent ones due to lack of knowledge regarding association, complex formation, etc. They are real deviations due to the

physical causes involved in what I have termed the thermodynamic environment.

PROF. W. LASH MILLER: I should like to ask Dr. Washburn why the two phases must be miscible in all proportions if the mol-fraction is the same for both. If a lump of ice is floating in a glass of water, the mol-fraction for each of them is unity, but the ice does not mix with the water.

PROF. WASHBURN: The equation applies only to two phases in the same state of aggregation.

PROF. MILLER: It seems to me that a new hypothesis is introduced by saying that if the two mol-fractions are the same, the two liquids must mix.

PROF. WASHBURN: If all the mol-fractions are the same in both phases, the solutions are identical in composition. This is a physical fact which is nothing more than our definition of identity of composition.

PROF. MILLER: I hardly think so. The mol-fraction gives the number of mols (not grams) of one chemical divided by the number of mols of the other in the same phase; hence to say that if the mol-fractions are equal, the gram-fractions must also be equal, is to assume that the mol-weights of the constituents are the same in both phases—or at least, that in one of the phases both constituents have mol-weights which are the same multiple of those in the other. Surely this is a "new hypothesis."

PROF. WASHBURN: We do not need to know what that divisor is. We may know nothing whatever about the values of the mol-fratcions of the different molecular species, but if they are the same in both phases the two phases must be identical (by definition). Therefore, they are the same phase.

I do not say that in any actual case we know what the mol-fractions are. For the demonstration I have just given, we do not need to know what these values are. I designated them simply by $x_a, x_b \ldots\ldots x_n$. My proof does not involve any knowledge of the particular numerical values of these quantities, for regardless of what they may be, they must be the same for each molecular species in both phases, if the equation,

$p = p_0 x$, holds. To deny this is to deny the Second Law of thermodynamics. And if they are the same for both phases then the two phases must be identical in composition by the very definition of identity of composition.

PROF. WASHBURN (*Communicated*): The present position of the theory of solutions may be concisely summed up by the following equation,

$$\pi = \varphi(x, T, M).$$

In this equation π is the osmotic pressure (or the partial vapor pressure, or the activity, or any one of the various thermodynamic potentials; according to the language in which one wishes to formulate his theory) for any molecular species in a solution in which its mol-fraction is x. T is the temperature and M the thermodynamic environment of the molecular species. In the most general case, M is a function of both x and T, the form of which is, in general, different for every solution. For this reason, the development of a universal theory of solutions in a workable form has not progressed very far nor does there seem to be any likelihood of very much immediate progress in this direction. The problem is very much simplified if we restrict ourselves to solutions in which M is a function of T only, being independent of x. For this case we have

$$\pi = \varphi'(x, T).$$

The effect of T upon π can be expressed thermodynamically in terms of purely thermal quantities capable of measurement in all cases and in this manner can be taken care of in any theory of solutions. The only question left, therefore, is to formulate the dependence of π upon x for T constant, and M independent of x. We have two large groups of solutions which come under this classification. They are (1) ideal solutions and (2) sufficiently dilute solutions. The first group includes solutions in which the two constituents of the solution resemble each other very closely. One of the most perfect examples of a solution of this character is one composed of two optical isomers dissolved in each other. The second group, sufficiently dilute solutions, includes solutions of any two substances, whatever, for it is evident that with continued dilution a point must eventually be

reached where the thermodynamic environment in the solution is indistinguishable from that which prevails in the pure solvent and is, therefore, practically a constant unaffected by further dilution. Since both of these groups are characterized by a thermodynamic environment which is independent of x, the form of the function

$$\pi = \varphi''(x)$$

will be the same for both of them and they will be governed by the same general set of laws. The form of this function is known and hence we are at the present time in possession of a comparatively extensive and satisfactory theory of solutions which includes all solutions of constant thermodynamic environment. If we formulate our function in terms of vapor pressure, it is

$$\left(\frac{d^2 p}{dx^2}\right)_{T,M} = 0$$

for each molecular species present in the solution. Starting with this equation, the whole set of laws governing both dilute and ideal solutions may be developed without any further assumptions, whatever, except the two laws of thermodynamics.

Dr. J. H. Hildebrand: I am in accord with Dr. Washburn in his contention that we dare not trust ourselves blindly to the vapor pressure law in its present form. It will be noted that in my communication I was quite content to say that *if* the vapor pressure law holds for zinc amalgams, then my measurements indicate polymerization of the zinc. I venture to hope, as I stated at the outset, that the series of similar measurements contemplated with other amalgams may shed some light both on the vapor pressure law itself, and on the constitution of liquid amalgams. I may add that in the following paper is presented a method whereby the law may be applied in an indirect, though quite rigid, way to molten alloys in general, by means of e.m.f. measurements. I have thought that the metallic solutions present perhaps the most promising field for investigating the theory of solutions, since they are relatively simple, and the results can be checked by our present accurate knowledge of the constitution of solid alloys.

A paper presented at the XXII General Meeting of the American Electrochemical Society, in Joint Session with Sections II: Inorganic Chemistry, Xa: Electrochemistry, and Xb: Physical Chemistry, of the VIII International Congress of Applied Chemistry, in New York City, September 9, 1912, Dr. W. Lash Miller in the Chair.

THE RELATION BETWEEN THE POTENTIAL OF LIQUID AMALGAM CELLS AND THE CONSTITUTION OF THE AMALGAM.

By Joel H. Hildebrand,

In 1891 G. Meyer published his well-known research[1] on the molecular weights of certain metals as determined by the potential of amalgam cells, drawing the conclusion that the metals investigated dissolved in mercury as atoms. In 1902 Haber[2] called attention to the fact that Meyer's measurements do not decide between the case of a metal dissolved in mercury as single atoms and that of a hydrargyrate of the composition MHg_m. By calculating the osmotic work necessary to transfer the solute from one amalgam to the other on the assumption of a hydrargyrate being formed, he showed how the ordinary formula must be modified, and calculated the extent of the effect on the potential. However, as the amalgams become more concentrated an additional and uncertain cause of deviation arises in the inexactness of the gas-laws as applied to osmotic pressure except at great dilution. Hence it is unsafe to refer to the formation of hydrargyrates all deviations from the simple concentration formula,

$$nEF = RT \ln \frac{c_1}{c_2}.$$

Haber proceeds to show that an exact expression can be given only in terms of vapor pressure, and, by analogy with the equation applied by Dolezalek[3] to the lead accumulator, gives the equation,

$$nEF = RT \left(w_2 \ln p_2 - w_1 \ln p_1 - \int_{w_1}^{w_2} \ln p \, dw + m \ln \frac{p_2}{p_1} \right)$$

[1] Zeit. phys. Chem., **7**, 477 (1891).
[2] Ibid., **41**, 399 (1902).
[3] Zeit. f. Elektrochem., **4**, 349 (1898).

In this expression n denotes the valence of the dissolved metal, E, the e.m.f.; F, the Faraday equivalent; R, the gas-constant; T, the absolute temperature; w, the number of mols of solvent mercury per mol of solute; p, the pressure of mercury vapor over the amalgams, and m the number of atoms of mercury combined with one atom of the solute metal. The subscripts, 1 and 2 refer to the concentrated and dilute amalgams respectively.

Now, it would appear from this equation that if p were known as a function of w, the expression could be integrated and the value of m determined, which would satisfy measured values of E. The question of solvation would be thus settled beyond the shadow of a doubt. A closer examination of the equation, however, shows that the value of m cannot be so determined, and that a method so free from objection for the determination of solvation is not involved in the equation.

If N denotes the number of mols of mercury present, including both solvent and solvate mercury, then, since

$$N_1 = w_1 + m, \text{ and } N_2 = w_2 + m,$$

the equation becomes,

$$nEF = RT\,(N_2 \ln p_2 - N_1 \ln p_1 - \int_{N_1}^{N_2} \ln p\, dN).$$

This will be more evident if the expression is derived directly, by a process of isothermal distillation.

Let us imagine two large reservoirs containing concentrated and dilute amalgams, I and II, respectively. We can transfer one atom of the solute metal, M, from I to II electrically, as in a concentration cell, whereby the work nEF would be gained. The same transfer may be made by isothermal distillation as follows.

1. Remove from I 1 mol MHg_m together with corresponding solvent mercury, $N_1 - m$ mols. This requires no work.

2. Distill into this portion from II enough mercury vapor to bring it to the same concentration as the amalgam in II. The amount distilled is $(N_2 - m) - (N_1 - m)$, or, $N_2 - N_1$, and the work done is

$$RT \int_{N_1}^{N_2} \ln \frac{p_2}{p}\, dN.$$

3. The separated portion is now of the same concentration as the amalgam in II and is added to it without doing any work.

4. We have now transferred from I to II $N_1 - m$ mols of solvent mercury and m of combined mercury, or N_1 mols altogether, in addition to 1 mol of the metal M. To make the process equivalent to the electrical transfer, we have finally to distill back into reservoir I N_1 mols of mercury, doing the work.

$$N_1 RT \ln \frac{p_2}{p_1}$$

Equating the total work done in the distillation process to the electrical work, we have,

$$nEF = RT \left(N_1 \ln \frac{p_2}{p_1} + \int_{N_1}^{N_2} \ln \frac{p_2}{p} \, dN\right) =$$

$$RT \left(N_2 \ln p_2 - N_1 \ln p_1 - \int_{N_1}^{N_2} \ln p \, dN\right).$$

It will be noticed that wherever m occurs it cancels out, and so does not appear in the final equation.

Now, this expression can be still further simplified by putting

$$\int \ln p \, dN = N \ln p - \int N \, d\ln p.$$

whence we obtain as the final form,

$$nEF = RT \int_{N_1}^{N_2} N \, d\ln p \,; \text{ or } nEF = RT \int_{N_1}^{N_2} \frac{N \, dp}{p}.$$

It must not be inferred from this that the potential of amalgam cells should be unaffected by the formation of hydrargyrates, for though m does not appear in the equation as given it is involved in any expression giving p as a function of N which we may use to integrate the final equation for e.m.f. here given by the writer.

We will now show how this equation can be integrated using the vapor pressure law to take into account the constitution of the amalgams involved.

Very accurate measurements of the potentials of amalgam cells have been made in recent years in the Harvard[4] and Prince-

[4] Richards and Forbes, Pub. Carnegie Inst., No. 56, and Zeit. phys. Chem., **58**, 683 (1907). Richards, Wilson and Garrod-Thomas, Pub. Carnegie Inst., No. 118, and Zeit. phys. Chem., **72**, 129, 165 (1909).

ton[5] laboratories. These measurements have shown that the gas-laws hold accurately at high dilutions, but that considerable deviations occur at greater concentrations, the direction depending upon the solute metal. Thallium, indium and cadmium give potentials greater, and zinc, lead and tin smaller than those calculated from the simple concentration formula. A number of methods of accounting numerically for these differences are used by Richards and his co-workers, but while the energy changes are rather well accounted for thermodynamically, the effect of polymerization or solvation is merely considered qualitatively, and that chiefly in the case of zinc, showing in a general way that the deviations are in the direction expected.

Let us suppose that the dissolved metal forms a solvate with the mercury of the general formula MHg_m. Then, if the solution is made from 1 mol of M and N mols of mercury, the solvent mercury would be N—m mols, and the total number of mols would be N—m+1. Using these values for the mol-fraction of mercury in the vapor pressure law,[6] which states that the pressure of a component over of a mixture is proportional to its mol-fraction in the mixture, the proportionality constant being the saturation pressure of the pure component p_0, we get the equation,

$$p = p_0 \frac{N - m}{N - m + 1}.$$

If this function of p in terms of N is used to integrate the general formula deduced above, the resulting equation is

$$E = \frac{2.3026RT}{nF}\left[m \log \frac{N_2 - m}{N_1 - m} - (m-1) \log \frac{N_2 - m + 1}{N_1 - m + 1}\right].$$

In applying this formula we will consider the case of thallium amalgams. Freezing point data have furnished definite evidence of the existence of the compound $TlHg_2$ in the solid state. In Table I are given the results of Richards and Wilson[7] on the potential of thallium amalgams at 30° compared with the results calculated from the ordinary concentration equation and from the equation just given, using for m the values 2, 5, and 6

[5] Hulett and DeLury, Journ. Am. Chem. Soc., **30**, 1812 (1908). Crenshaw, J. phys. Chem., **14**, 158 (1910).

[6] Cf. preceding paper.

[7] *Loc. cit.*

successively. It will be seen that the value $m = 2$ improves the agreement with the measured potentials considerably, but a much better agreement is gotten from the value 5 or 6.

We must conclude from this that dilute thallium amalgams contain the compound $TlHg_6$. It will be interesting to confirm this by means of measurements of vapor pressure of thallium amalgams.

TABLE I.

Percent Tl	N	Potential in millivolts at 30°				
		Observed	Calculated from			
			c_1/c_2	$TlHg_2$	$TlHg_5$	$TlHg_6$
1.8456	54.2	37.13	32.78	34.42	36.60	37.42
0.5249	193.5	22.61	22.61	21.90	22.32	22.52
0.2294	443.5					

Let us now apply to the fundamental equation for e.m.f. the vapor pressure measurements made by the writer[8] on zinc amalgams. It has been shown that the vapor pressures of zinc amalgams are given quite accurately by the equation,

$$\frac{p}{p_o} = \frac{2N\,(K+4)}{N\,(K+8) + K + 4 + \sqrt{(KN+K)^2 + 4K\,(2N+1)}},$$

where K is the equilibrium constant of the reaction,

$$2Zn = Zn_2,$$

as given by the equation,

$$\left(\frac{1-2\alpha}{N+1-\alpha}\right)^2 = K\,\frac{\alpha}{N+1-\alpha},$$

in which α represents the number of mols of Zn_2 produced. α is gotten in terms of K and substituted in the vapor pressure law which, in this case, is expressed as

$$\frac{p}{p_o} = \frac{N}{N+1-\alpha}.$$

[8] Cf. preceding paper.

In order to integrate the expression

$$nEF = RT \int_{N_1}^{N_2} N d\ln p$$

we can write, since α is small when N is large, a condition fulfilled in the e.m.f. measurements we shall use,

$$\frac{I}{N} = K\alpha$$

If the value $K = 0.50$ holds at lower temperatures then

$$\frac{p}{p_o} = \frac{N}{N + 1 - \frac{2}{N}},$$

and

$$\frac{p}{p_o} = \frac{N^2}{N^2 + N - 2}.$$

Using this equation in the above integration, we get for the e.m.f. of zinc amalgams

$$E = \frac{2.3026RT}{2F}\left(2 \log \frac{N_2 + 2}{N_1 + 2} - \log \frac{N_2 - 1}{N_1 - 1}\right)$$

To test this equation we have both the measurements of Richards and his co-workers[9] and those of Crenshaw.[9] Table II gives observations of Richards and Garrod-Thomas on the potential of the most concentrated amalgams used. Compared with the observed values are given those calculated from the ratio c_1/c_2 and from the equation just derived by the writer.

In Table III are given similar figures for the amalgams measured by Crenshaw, which extend to much higher concentrations, where the deviations from the gas-law equation are very great. Here again, however, the potentials calculated from p are in excellent agreement with the observed potentials, the slight deviations being in the direction produced by the simplifying assumptions made in integration.

It may seem strange that the value of K obtained at 300° should apparently remain the same at ordinary temperatures. It is by no means impossible, even though somewhat unusual. The constancy of K is borne out in a rather imperfect way by the

[9] *Loc. cit.*

vapor pressure measurements. The ratio p/p_0 seemed to be independent of temperature, although careful measurements of this ratio at a widely differing temperature have not yet been made.

It must be emphasized, finally, that even though it were shown that the experimental values of the relation between p and N are not due to association of zinc atoms, nevertheless, the course of the vapor pressure curve, and therefore the potentials calculated from it, remain the same, and therefore in agreement.

It may be concluded, therefore, that the equation here given by the writer is confirmed by the behavior of zinc, and the probable behavior of thallium amalgams. The writer hopes soon to be able to report measurements upon thallium and other amalgams.

TABLE II.

Percent Zn	N	Potential in millivolts at 30°		
		Observed	Calculated from	
			P	c_1/c_2
0.900	36.0	10.18	10.18	11.13
0.384	84.9	6.12	6.18	6.45
0.234	139.4			

TABLE III.

grams Zn / grams Hg	N	Potential in millivolts at 25°		
		Observed	Calculated from	
			P	c_1/c_2
2.20/100	14.86	0.89	0.87	1.34
2.00/100	16.36	0.94	0.98	1.35
1.8 /100	18.17	2.43	2.48	3.23
1.4 /100	23.35	3.54	3.57	4.32
1/100	32.70	7.83	7.93	8.90
5/1000	65.37			

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DISCUSSION.

DR. G. S. FORBES: I apologize for taking up the time of the Section again. I would say that while very properly in agreement with the general principles of Dr. Hildebrand's conclusions, I see in the equations for electromotive force no provision for the transformation of at least part of the heat of dilution into electrical energy. I would ask whether, if such a heat of dilution exists, it would not be necessary to correct π for that portion of it which is not bound energy.

DR. J. H. HILDEBRAND. The fundamental equation is deduced by means of an isothermal process in which the heat of dilution does not and should not appear. In Cady's equation the heat term is introduced as a sort of makeshift because the term

$$RT \ln \frac{c_1}{c_2}$$

does not give accurately the osmotic work done in expanding the solute between the concentrations c_1 and c_2. This is true whenever apparent concentration does not vary with the osmotic pressure according to the gas law, $P = RTc$. On the contrary, the work represented by the right hand member of the equation given in my paper,

$$RT \int_{N_1}^{N_2} N d\ln p,$$

is the maximum work, and must equal, without further correction, the work done in the electrical transfer, provided only that the vapor obeys the gas laws. Even this limitation is removed if, instead of vapor pressure, we consider fugacity, in accordance with the suggestion of Prof. G. N. Lewis applying to such cases.

The only room for doubt is, I think, in connection with the assumption used in integration, *i. e.*, that the vapor pressure, or fugacity, is proportional to the mol-fraction of the solvent mercury. It is quite conceivable that this may require modification, although such modification would in no wise interfere with the utility of the e.m.f. formula. It would necessitate only a different integration.

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THE ELECTROCHEMICAL BEHAVIOR OF VERY CONCENTRATED THALLIUM AMALGAMS.

By Theodore W. Richards and F. Daniels.

In continuation of previous work on this subject by one of the authors and Dr. J. H. Wilson, the electromotive forces between liquid amalgams of thallium of great concentration were carefully studied at various temperatures. From the temperature coefficients of these concentration cells the heats of dilution were calculated. It was found in every case that the observed electromotive forces greatly exceeded those calculated from the concentrations alone. Thus for example in the case of a cell made from amalgams of 3.736 percent and 21.722 percent thallium respectively, an e.m.f. of 76.3 milli-volts at 30.00° C. was observed while the concentration effect would be only 45.3 milli-volts. If to the concentration effect (theoretical) is added the e.m.f. calculated from the heat of dilution, according to the equation of Cady

$$\left(\pi = \frac{Q}{nF} + \frac{RT}{nF} \ln \frac{C_1}{C_2}\right) .$$

the agreement is much better. Thus the quantity $\frac{Q}{nF}$ in the case cited above was 40.4 milli-volts, and the sum is 85.7. The *excess* (9.4 milli-volts) of this sum over the observed value, may perhaps be ascribed to partial *association* of the atoms of thallium in concentrated amalgams.

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THE INCLUSIONS IN ELECTROLYTIC SILVER AND THEIR EFFECT ON THE ELECTROCHEMICAL EQUIVALENT OF SILVER.*

By J. S. Laird and G. A. Hulett.

Introduction.

In their classic memoir on the electrochemical equivalent of silver, Rayleigh and Sedgwick[1] were the first to raise the question as to whether the deposit in the silver coulometer was pure silver or not. They were led to raise this question by the fact which they observed that the deposits from a silver nitrate solution which contained a little silver acetate were quite different in appearance, finer and more coherent and gave a higher value for the electrochemical equivalent of silver than deposits from silver nitrate solution free from acetate. Since then many investigators have considered this question, and have left it in almost the same state that Rayleigh and Sedgwick did. As the present research was designed to clear up this old problem, and as it is based upon principles quite different from those employed in any of these previous researches, with the exception of the work of Hulett and Duschak,[2] a brief critical review of this previous work seems to be in order.

Rayleigh and Sedgwick used in their researches only one form of coulometer, that which has come to be known as the Rayleigh form, consisting of a platinum dish which served as cathode, as anode a disc of fine silver wrapped with filter paper to retain the anode slime, and a solution of silver nitrate as electro-

* The work described in this article was made possible by a grant from the Elizabeth Thompson Science Fund, which placed at our disposal some of the special apparatus and materials needed for this investigation, and the authors take pleasure in acknowledging their indebtedness to the Trustees of this Fund.

[1] Rayleigh and Sedgwick, Phil. Trans., **175**, 111.

[2] Hulett and Duschak, Trans. Am. Electrochem. Soc., **12**, 257 (1907).

lyte. They seem to have taken no precautions to purify their electrolyte. As stated, the difference in the deposits caused by the presence of a small quantity of silver acetate first led them to question the purity of the silver deposits. They attempted first of all to decide this question by direct analysis of the deposits. The method used was solution of the deposits in nitric acid, precipitation with sodium chloride solution, and comparison of the amounts of silver chloride obtained with the amounts obtained from known weights of pure silver obtained from Johnson and Matthey. There was no apparent inferiority in the deposits beyond 0.017 percent. Later they attempted to drive out the volatile part of the inclusion by heating the deposits and determining the loss in weight. To this end they heated the coulometer cups containing the deposits to incipient redness over a Bunsen burner. In a large number of experiments silver deposits of between two and three grams lost in weight on being heated in amounts up to 0.7 mg., averaging in 21 experiments 0.15 mg., or about 0.007 percent. Deposits from silver nitrate solutions containing silver acetate lost much more when heated, in one experiment 2.9 mg., in another 1.3 mg., or on the average 0.1 percent.

T. Gray[3] states, without giving any experimental data, that silver deposits which have been insufficiently washed become brighter and decrease in weight when heated. Deposits which have been properly washed may be heated without appreciable loss in weight.

Richards, Collins and Heimrod[4] analyzed a number of silver deposits formed in the porous cup coulometer from pure silver nitrate solutions. They dissolved the deposits in nitric acid, and precipitated the silver with pure hydrobromic acid, taking all the precautions observed in atomic weight determinations in the Harvard laboratory. G. Van Dijk[5] has pointed out two arithmetical errors in the table of results as published. The corrected results are given in the following table:

[3] Gray, Phil. Mag., 22, 399.

[4] Richards, Collins, and Heimrod, Proc. Amer. Acad., 35, 133.

[5] Van Dijk, Ann. der Phys., 19, 246.

Silver Taken	Silver Bromide Obtained	Silver Calc. from Silver Bromide	Deficiency in Silver	Percent Deficiency
0.71585	1.24567	0.71558	+0.00027	+0.040
5.43807	9.46557	5.43747	+0.00060	+0.011
3.76993	6.56216	3.76961	+0.00032	+0.008
2.29649	3.99820	2.29674	—0.00025	—0.011
2.15701	3.75473	2.15689	+0.00012	+0.006
2.37893	4.14187	2.37928	—0.00035	—0.015
2.97120	5.17218	2.97114	+0.00006	+0.002
			Mean deficiency . .	+0.006

It appears that two of the results are negative and five positive and that the average deficiency is .006 percent, but this is not much greater than the probable error of the series, which we calculate to be .0036 percent. The deficiency in the first determination (.040 percent) is about four times as great as the probable error of a single determination and as a relatively small amount of silver was used in this determination it seems to be questionable. If we leave out the first result the average deficiency of the remaining six is .0003 percent, or much less than the probable error. These results give no information as to the amount of inclusion, in fact they would hardly justify an assertion that there was any impurity in the electrolytic silver.

Later Richards and Heimrod[6] followed Rayleigh's second method, and determined the loss in weight suffered by silver deposits when heated to constant weight over an alcohol lamp. In each determination the loss in weight was corrected by 0.1 mg. for the loss of platinum from the crucible. They observed decreases in weight varying from 0.06 mg. to 0.5 mg. on deposits of from 1.6 to 2 grams, the average loss in twelve experiments being 0.018 percent.

G. Van Dijk[5] made a careful study of the effect of heat on silver deposits. He heated his platinum crucibles with adherent deposits to about 500° C., in a porcelain-tube resistance furnace, to avoid the effects of burner gases. Out of seven experiments, in two there was a decrease in weight, in the others a slight increase, the average decrease for the series being +0.0004 percent. He therefore concluded that deposits from pure silver nitrate solution on platinum contained no appreciable amounts of

[6] Richards and Heimrod, Proc. Amer. Acad., 37, 435.

inclusion. He found, however, that deposits on old glowed deposits of silver did lose weight when heated.

In their very extensive research on the silver coulometer Smith, Mather and Lowry[7] barely considered the possibility of there being liquid inclusions in the deposits. They simply accepted Van Dijk's conclusion, after verifying it to the extent of heating deposits on silver bowls over a Bunsen burner on three occasions to a red heat without observing any loss in weight.

Jaeger and von Steinwehr[8] heated a number of silver deposits on platinum crucibles over a Bunsen flame to incipient redness. They observed small decreases in weight, in most cases amounting to some hundredths of a milligram on about two grams deposit. The decreases were not as great, however, as those suffered by the empty crucibles when similarly heated. They concluded that there could be no appreciable amount of inclusion in the deposits.

A study of the literature (quoted above) shows that all previous attempts, with the exception of the work of Hulett and Duschak,[2] to determine the amount of impurity in silver coulometer deposits have been carried out according to the two methods introduced by Rayleigh and Sedgwick.

First. Direct analysis of the silver.

Second. Determination of the loss in weight which the deposits, previously heated to 160° C. in the regular manipulation, suffer when heated to redness in the platinum cup.

The analyses of Rayleigh and Sedgwick were so inaccurate as to merit only passing reference. The later work of Richards and Collins makes much greater claims to accuracy, but a critical examination of the results gives no information on the inclusions in electrolytic silver.

The loss in weight suffered by silver deposits when heated would be due to the included water, to the NO_3 of occluded silver nitrate and to decomposition of any organic colloid which was deposited with the silver. Rayleigh and Sedgwick simply heated their deposits over a Bunsen burner, where there was danger of contamination by the gases of combustion. Although they worked with a comparatively impure solution, they sometimes observed no loss on heating, but more often a decrease of a few

[7] Smith, Mather, and Lowry, Phil. Trans., **207**, 570.
[8] Jaeger and von Steinwehr, Zeit. f. Instr., **12**, 354.

tenths of a milligram. Richards, Collins and Heimrod heated their deposits over an alcohol lamp, as its flame would not contain sulphur gases as a gas flame does; in each case there was a decrease in weight, amounting on the average to 0.018 percent.

Van Dijk's work is much more careful. He used an electric furnace for heating his deposits, so that there could be no question of contamination by flame gases. The few attempts of Smith, Mather and Lowry were made with little care, at low temperatures, and are not of much value. Jaeger and von Steinwehr's experiments were much like those of Rayleigh and Sedgwick, but gave negative results.

A study of all the work done by the second method of Rayleigh and Sedgwick shows that the results are contradictory and that there is no reliable evidence of electrolytic silver suffering a loss when heated to incipient redness in an open dish. If the loss could be accurately determined, the results could not be interpreted since the inclusions are silver nitrate, water and colloidal organic matter and one does not know the relation between the volatile constituents in determining only the total loss, or how completely the volatile constituents have been expelled. Hulett and Duschak found that, even when electrolytic silver was heated in a vacuum, little was given off at 400° and not all of the volatile constituents were eliminated until the silver was melted, so we would hardly expect that the method of heating electrolytic silver in an open dish to incipient redness would eliminate any considerable portion of the volatile inclusions. Hulett and Duschak approached the problem in quite a different way. In their experiments the deposits scraped off the platinum cathodes were placed in a hard glass tube connected with a mercury manometer and provided with a calibrated side tube in which the water could be condensed and measured. The whole apparatus was carefully exhausted and sealed off. The silver investigated had been deposited from a solution of Kahlbaum's silver nitrate. They found in four experiments an average of 0.09 mg. of water per gram of silver, and a small quantity of some other gases, which they assumed to be oxygen and oxides of nitrogen formed by the decomposition of silver nitrate and corresponding to 0.041 mg. silver nitrate per gram silver. In the experiments the deposits were heated slowly, the temperature being raised by suc-

cessive steps. It was found that the deposits did not lose all their volatile constituents at one definite temperature. Below 400° C. nothing but small amounts of water vapor were given off. Above this temperature both gas and water vapor were given off, with each rise in temperature a certain amount being given off, and then no more until the temperature had been again raised. With each increase in temperature there was a corresponding increase in pressure, which attained a definite value and remained constant as long as the temperature remained constant. Apparently at each temperature a definite quantity of gas and water vapor was eliminated from the silver in a short time, and no more until the temperature had been again raised. This would seem to indicate that the impurity was uniformly distributed throughout the silver, a higher pressure, produced by a higher temperature, being necessary to drive out the volatile constituents from the inner recesses of the crystals.

This work is very valuable as being the first direct evidence that electrolytic silver does contain measurable amounts of impurity. Our preliminary work showed, however, that it is impossible to heat an evacuated glass or quartz apparatus without the walls of the glass or quartz giving off gases. This fact introduces a slight uncertainty into the above results. At the commencement of this work it was planned simply to extend the work of Hulett and Duschak to the melting point of silver, as they had shown in one experiment that the silver retained part of the volatile constituents until it was melted. To enable us to reach this temperature, a quartz tube was substituted for the hard glass tube used by Hulett and Duschak. Difficulties were immediately encountered, as the melted silver on cooling always froze to and cracked the quartz tube. This difficulty was avoided by putting the silver in quartz boats, made by sealing both ends of a piece of quartz tubing of suitable size and grinding off one side. Quite anomalous results were obtained, the quantity of gases evolved depending apparently on the length of time of heating. A partial explanation of this phenomenon is probably to be found in the fact which has been pointed out by Fischer and Tiede[10] and by Richardson[11] that quartz is somewhat permeable to certain gases at high temperatures. Also it is possible

[10] Fischer and Tiede, Ber. Deut. Chem. Gesell., **44**, 1711.
[11] Richardson, Phil. Mag., **22**, 704.

that gases condensed on the surface of quartz are only given off at high temperatures. Attempts were also made to determine the loss in weight suffered by deposits when melted. The deposits were heated to the melting point in a weighed quartz tube exhausted by a mercury pump, but no accurate results could be obtained, as the surface of the quartz crystallized quite rapidly at the high temperature and flaked off. So this method was abandoned.

The problem was now attacked from an entirely new direction, *viz.*, by the use of a metallic solvent which would dissolve the silver but not the included impurity. The water or other gaseous impurity, being insoluble in the liquid metal, would be freed from the silver at a low temperature, and could then be analyzed. This, it may be noted, is a direct method of separating out and determining the impurities. There is here the possibility of working at comparatively low temperatures and so avoiding the difficulties involved in connecting hard glass or quartz tubes to an apparatus of ordinary glass by means of ground joints. The sources of error mentioned above are also avoided. Mercury naturally suggests itself as a metallic solvent, but the solubility of silver in mercury is quite small, only about one part in one hundred at the boiling point of mercury. Silver is, however, quite soluble in molten tin at a fairly low temperature. The two form a eutectic mixture containing 3.5 percent silver which melts at 232° C. With rising temperature the solubility rises rapidly, being 50 percent at 500° C., and it was found that when small quantities of silver are added to a mass of molten tin at a temperature of 400° or 500° C. they dissolve almost instantly, with the elimination of any gaseous inclusion. Tin is readily oxidized at this temperature, and not only takes up oxygen rapidly and completely, but also reduces oxides of nitrogen, even nitric oxide being reduced to nitrogen. It also decomposes silver nitrate, the silver and oxygen being retained and the nitrogen liberated quantitatively. These points were very carefully tested out experimentally.

Apparatus.

The apparatus finally employed in the determinations is shown in the accompanying diagram (Fig. 1). The whole apparatus was made of ordinary glass, all the parts being fused together

so that it was free from joints, and the only stop-cock was one in the manometer, so arranged that it could not possibly leak or introduce organic material into the apparatus. This important point is taken up more in detail in the description of the manometer.

The tin, which had been previously purified and heated to a high temperature in a vacuum, was contained in the bulb *A*, which could be heated in an electric furnace. The weighed sample of silver was placed in the platinum boat *B* outside the furnace. It was introduced through the tube *C*, which also served as a connection to the mercury pump. There was also sealed on the small bulb *D* containing a copper oxide glower, which was made as follows: A coil of 0.15 mm. platinum wire was wound on a small quartz tube and enclosed in another quartz tube which fitted it closely. Fine copper wire was wound on the outside of the outer tube. Heavy platinum leads were gold-soldered to the ends of the platinum coil and fused through the containing glass bulb. The resistance of the platinum coil was about four ohms, and on passing a current of two amperes through it the whole was heated to redness. The coil was first glowed in air until the copper became covered with an adherent layer of copper oxide, and was then thoroughly glowed in a vacuum. This copper oxide glower served in the analysis to oxidize any hydrogen or other reducing gases which might be liberated from the silver. The slender tube *E* could be immersed in a freezing mixture or liquid air and served in analysis of the gases by the method of fractional condensation. The small capillary tube *F*, which was drawn out to a fine point and sealed, was used in finally measuring the volume of the apparatus.

The Manometer. A very important part of the apparatus was the manometer used for measuring the small gas pressures. A mercury manometer was the only kind possible, as no other liquid has as low a vapor pressure or can be depended on not to dissolve gases or give them up to a vacuum. The meniscus of a falling column of mercury is quite different from that of a rising column, so that accurate measurements can only be made with an adjustable manometer in which the mercury can be made to rise in both tubes before the difference in levels is measured. In our work the volume of the apparatus had to be determined in

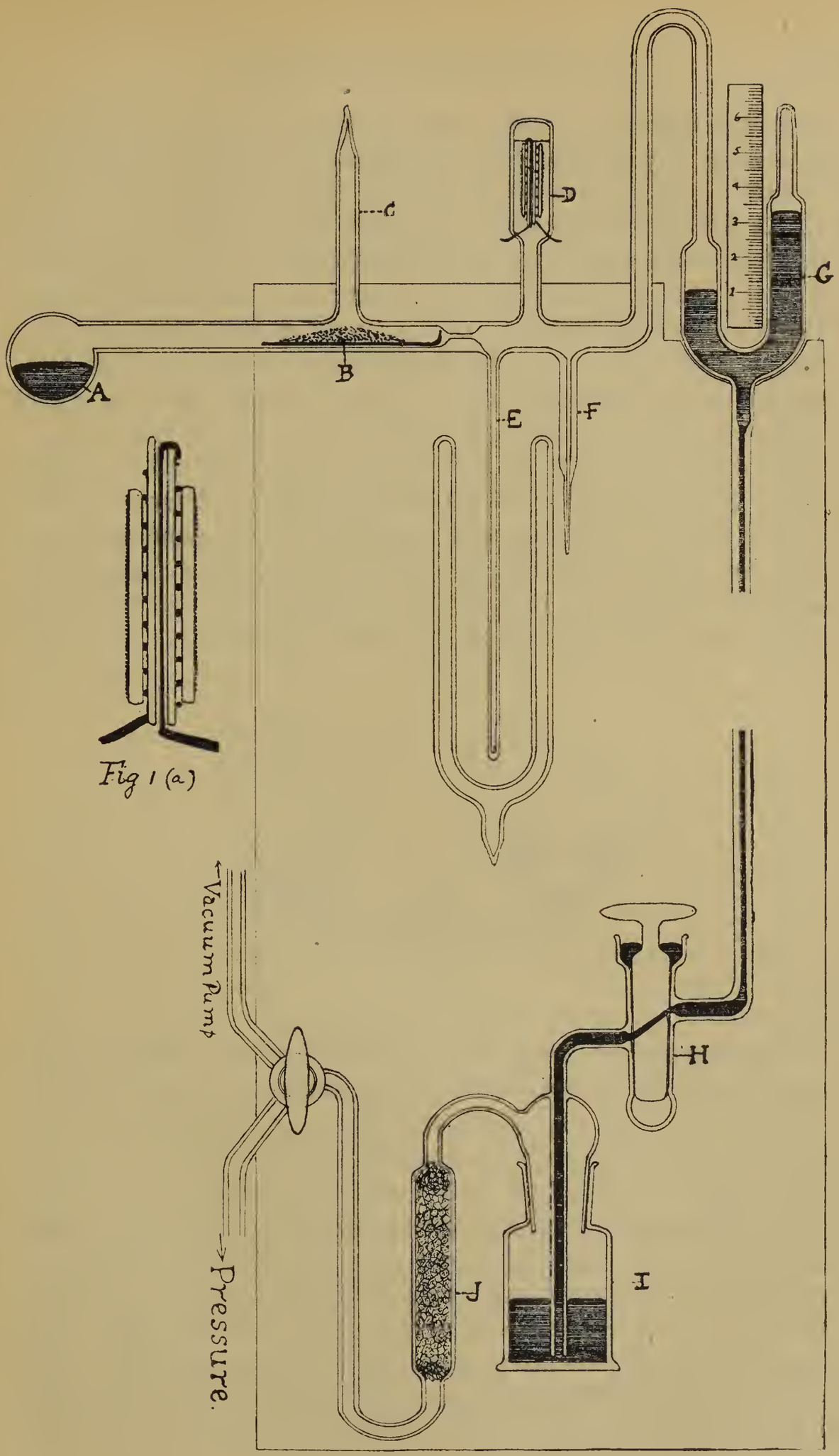

Fig 1 (a)

FIG. 1.

each experiment, and this could only be done conveniently by measuring the volume of air required to fill it at atmospheric pressure. As the volume had to be the same when filled with air at atmospheric pressure as when there was only a small pressure in the apparatus, the manometer had to be so constructed that the mercury meniscus in the arm connected with the apparatus could be adjusted to and held at any given point no matter what the pressure in the apparatus might be. The manometer used in the earlier part of this work consisted of a *U* tube connected by a capillary tube, sealed on at the bottom and provided with a stop-cock, to a mercury reservoir closed by a stop-cock. The air pressure on the mercury in the reservoir could be varied at will, and thus the mercury in the manometer was adjusted to any desired height and held there free from atmospheric disturbances by closing the stop-cock in the connecting tube, thus avoiding tubes of barometric height.

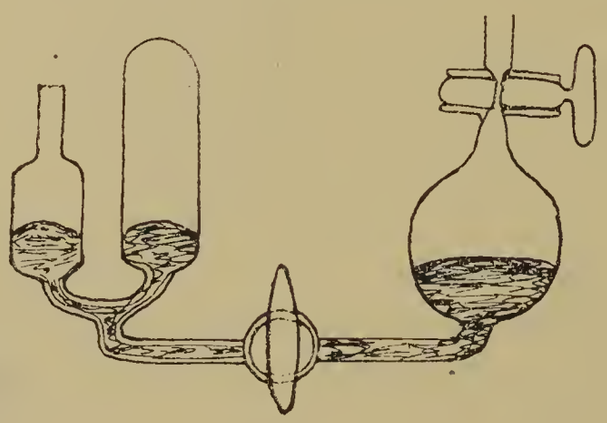

FIG. 2.

This simple and compact form of manometer fulfilled all the requirements, but it was found in practice that a trace of the fat required to keep the stop-cock tight was sometimes carried by the mercury into the manometer, so that the mercury and tubes soon became dirty and accurate readings were impossible. Whatever vapor was given off by the fat contaminated the gases in the apparatus, and also any moisture which condensed on the mercury in the reservoir soon crept along the connecting tube as the mercury levels were adjusted until it was given up to the evacuated apparatus. These difficulties finally led us to modify the manometer by carrying the connecting tube down almost 76 cm. below the *U* before inserting the cock *H* as

shown in Fig. 1. Being under such slight difference in pressure, a mercury seal was found to prevent leakage entirely, and the cock worked perfectly without any fat at all, with simply a little graphite to keep it from sticking. The end of the tube dipped under mercury in a small Drexel bottle *I*, which served as mercury reservoir and was connected through the calcium chloride tube *J* with a three-way cock *K*, communicating either with a vacuum pump or with an air-pressure supply. With this manometer there has never been the slightest suggestion of a leak, and the mercury and manometer tubes have remained quite bright and clean. The larger tubes of the manometer were 1.5 cm. internal diameter, the smaller ones at the top 0.5 cm. Convenience in manipulation was attained by mounting the apparatus and manometer together on a suitable stand. A steel scale was hung between the arms of the manometer, and the heights of the mercury columns compared with it by means of a cathetometer provided with a micrometer eye piece.

Method of Analysis.

The quantities of gases evolved when electrolytic silver is dissolved in tin are small, and require a special method of analysis. The one adopted was that of fractional condensation. The only gases which could be present were water vapor, nitrogen, carbon monoxide and dioxide, hydrogen, and possibly some hydrocarbons. The water vapor was condensed by a freezing mixture with a temperature of —70° C. The carbon dioxide was condensed by liquid air, its vapor pressure at —180° being less than 0.001 mm. The only other gases which might be condensed at this temperature were higher hydrocarbons, which could hardly have been present under the conditions of the experiments. The other gases, with the exception of the nitrogen, were oxidized to water and carbon dioxide, and condensed as such. The nitrogen, which alone remained uncondensed, could only have come from the decomposition of silver nitrate, and was taken as a measure of the silver nitrate originally present in the silver crystals.

The deposits studied were those obtained by Mr. Buckner in his work on the silver coulometer (this volume, page 367). The carefully washed and dried deposits, after they had been weighed,

were scraped off the platinum cups with a platinum spatula and sealed off in previously-glowed glass tubes, great care being taken to avoid contamination by dust. The sample of silver under investigation was weighed and introduced into the platinum boat *B* through the tube *C*. This tube was then connected to a mercury pump by means of a glass tube drawn out quite near the apparatus to a thick capillary. The whole apparatus was now carefully exhausted; at the same time the tin bulb inside the furnace was heated to 500° C., and the copper oxide glower heated to redness. This obviated the possibility of gases being given off later by the tin, or glower, or from the heated parts of the glass. The exhaustion occupied about an hour, so there was ample opportunity for any surface moisture to be absorbed by the phosphorous pentoxide. The pressure was reduced to about 0.003 mm., and then the connecting capillary was fused off by means of a hand blow-pipe. The apparatus now being hermetically sealed, the glower was allowed to become cold, and the whole apparatus on its stand was tilted and jarred, so that the silver ran down into the molten tin, where it was immediately dissolved. The bulb with the tin and silver was heated to 500° C. for about an hour, after which it was allowed to cool down to room temperature. One batch of tin, amounting to about 60 grams, was used for about eight successive samples of silver.

The volume of the apparatus was such that the water liberated from a 5-gram sample of silver was always well below its saturation pressure. When the apparatus had cooled to room temperature the total pressure was measured with the mercury adjusted to a definite point in the open arm of the manometer. The condensing tube *E* was now immersed in a freezing mixture consisting of solid carbon dioxide and ether, or, more usually, of alcohol cooled to —70° C. by the addition of liquid air. At this temperature the vapor pressure of water is less than 0.003 mm. The residual pressure was now measured, and as it was small the manometer was used as a McLeod gauge by allowing the gases to enter the closed arm of the manometer and compressing them into a measured volume in the narrow tube, the compression being 11 to 1, and the observed difference in level 7.1 times the true pressure. The freezing mixture was now replaced by liquid air, and the pressure again measured, the decrease below

the last reading being due to the condensation of the carbon dioxide. Leaving the side tube still in liquid air, the copper oxide was glowed until there was no further decrease in pressure, any hydrogen, carbon monoxide or hydrocarbons being oxidized to water or carbon dioxide and condensed, and the residual pressure being due to nitrogen. The liquid air was now removed, and the whole apparatus allowed to come to room temperature again. The total pressure was again measured, using the simple manometer and correcting for the small pressure of nitrogen in the right arm of the manometer. Lastly the freezing mixture was applied again and the amount of water redetermined. The volume of the apparatus was determined by connecting the filed end of the capillary tube *F* to a burette, filled with air over water, by means of a stout rubber tube. The tip of the capillary was broken off inside the tube, and the volume of air which entered from the burette gave a measure of the volume of the apparatus. The reading was, of course, corrected for the small pressure of gas already in the apparatus, and the mercury meniscus brought to the same point in the open arm of the manometer where it was when the pressures were measured. A complete determination usually occupied about six hours.

Results.

It was originally planned to run these determinations of the inclusions in the silver deposits concurrently with Mr. Buckner's researches on the silver coulometer, with the idea that it might be possible to explain the differences in the weights of deposits formed from different solutions, or under different conditions, on the basis of differences in the inclusions. Unfortunately the final satisfactory method of analysis was not worked out until after a great many samples of electrolytic silver had been used up in experimentation, or only incompletely determined, so it is only with the last samples investigated that we were able to trace anything like a quantitative relation between two variations. The determinations up to run 20 give only the water content of the silver and the volume of residual gas after the water vapor had been condensed, without giving any idea of the composition of this residual gas, for it was not until this stage of the work

that we discovered the existence of oxidizable gases in this residual gas and began to use the copper oxide spiral; the results, however, as determined and given in the following tables do show that silver, deposited from even the purest silver nitrate solution, always contains appreciable amounts of inclusions, and that the amount varies greatly with differences in the conditions under which it has been deposited, and in particular with differences in the purity of the electrolyte.

In his first eleven coulometer runs, Mr. Buckner had in series two platinum and two gold cups, provided with porous cups to keep the catholyte free from anode liquor, and as electrolyte a 15 percent solution of the purest silver nitrate he could prepare. There was sometimes also in series a Rayleigh coulometer with the anode wrapped in filter paper, and as electrolyte a 15 percent solution of Kahlbaum's silver nitrate. The analyses of the deposits as far as they were obtained are given in Table I.

Averaging these results from run 5 to run 11, and excluding the determination made by melting the silver in quartz, which is only put in for purposes of comparison, we get:

	Platinum	Gold	Rayleigh
Mg. Water per Gram Silver	0.040 ± 0.002	0.037 ± 0.003	0.051 ± 0.0035
Mm. Residual Gas per Gram Silver	16 ± 1.8	24 ± 3.5	50 ± 10

These results show that the deposits on the gold cups contained slightly less water than the deposits on the platinum cups, but that the other impurities were considerably greater in the deposits on gold. The water in the Rayleigh coulometer silver was 0.011 percent more than in the silver deposited from the pure solution, while there was more than three times as much uncondensed gases. Mr. Buckner found the deposits on gold to be 0.012 percent heavier than those on platinum, while the deposits in the Rayleigh coulometer were 0.030 percent heavier.

In the runs from 11 to 20 Mr. Buckner had in series two platinum cups, the one containing his purest silver nitrate solution, the other a solution of Kahlbaum's silver nitrate recrystallized from a solution acidified with a little nitric acid and fused.

The anolyte was separated from the catholyte by a porous cup. In the last four runs a Rayleigh coulometer was also in series, and contained the same electrolyte as the second platinum cup. We have only a few partial analyses of these deposits.

TABLE I.

Description of Deposit	Mg. Water per Gm. Silver	Cu. mm. Residual Gas per Gm. Silver	Remarks
On platinum .. Run 2.	0.061	28	Silver and tin melted together.
On platinum .. Run 3.	0.054	18	" " " " "
Platinum cup 1 Run 4.	0.053	27	" " " " "
Platinum cup 2 Run 4	0.049	35	" " " " "
Gold cup ..... Run 4.	0.044	40	" " " " "
Platinum cup . Run 5.		14	Melted tin before adding silver.
Gold gauze ... Run 5.	0.043	16	" " " " "
Platinum cup . Run 6.	0.033	56	Melted in quartz.
Rayleigh ..... Run 6.	0.044	25	Dissolved in melted tin.
Platinum cup . Run 7.	0.049	21	" " " "
Rayleigh ..... Run 7.	0.044	30	" " " "
Platinum cup . Run 8.	0.035	22	" " " "
Gold cup ..... Run 8.	0.049	35	" " " "
Rayleigh ..... Run 8.	0.050	54	" " " "
Platinum cup . Run 9.	0.041	15	" " " "
Gold cup ..... Run 9.	0.027	27	" " " "
Rayleigh ..... Run 9.	0.066	92	" " " "
Platinum cup . Run 10.	0.043	7	" " " "
Gold cup ..... Run 10.	0.034	10	" " " "
Platinum cup . Run 11.	0.040	13	" " " "
Gold cup ..... Run 11.	0.033	25	" " " "

TABLE II.

Description of Deposit	Mg. Water per Gram Deposit	Cu mm. Residual Gas per Gram Silver
Kahlbaum's silver nitrate, run 12	0.064	17
"Normal" silver nitrate, run 14	0.042	15
Kahlbaum's silver nitrate, run 14	0.046	26
"Normal" silver nitrate, run 15	0.040	3
Kahlbaum's silver nitrate, run 15	0.044	30
Kahlbaum's silver nitrate, run 16	0.084	48
Kahlbaum's silver nitrate, run 17	0.072	20
Kahlbaum's silver nitrate, run 20	0.087	72
"Normal" silver nitrate, run 20	0.033	10
Rayleigh coulometer, run 20	0.115	31

Averaging these results we get:

	Normal	Kahlbaum	Rayleigh
Mg. Water per Gram Deposit	0.038 ± 0.002	0.066 ± 0.005	0.115
Residual Gas in Cu. mm. per Gram Deposit	9 ± 2	35 ± 5.5	31

The silver deposited from the Kahlbaum silver nitrate contained 0.028 percent more water and about three times more of other impurity than the silver deposited from the purest silver nitrate. Mr. Buckner found the deposits from the Kahlbaum silver nitrate solution to be 0.009 percent heavier than those from the normal solution. The Rayleigh coulometer deposit is, again, very much more impure than the others. In run 20 the deposit in the platinum cup from the Kahlbaum silver nitrate was very peculiar, being quite slimy in appearance. The impurity in the deposit is correspondingly high.

The last set of results (see following table), in which the analysis was as complete as we were able to make it, is given as obtained, being simply figured to a common basis of cubic millimeters of gas per gram silver under standard conditions. This is necessary, as we have not yet succeeded in completely interpreting all of our results. In particular it may be noted that in some cases the total volume of gas after glowing the copper oxide is less than before the oxide was glowed. We cannot give any explanation for this peculiarity, which was most noticeable in the case of the Rayleigh deposits.

TABLE III.

Cubic Millimeters Gas.

Mm.³ Gas Experiment	Total	Cond. −70 °C	−70 °C	Cond. −180 °C	−180 °C	Ox. and Cond.	+Ox. −180 °C	Total	Cond. −70 °C	−70° C	Percent
Plat. Cup II, Run 24...	140.7	102.1	38.62	8.96	29.66	28.50	1.16	141.7	134.1	7.65	Alundum Best, I + .0007; III + .0047; IV + .0061
Gold Cups, Run 24.....	124.3	98.4	25.84	4.56	21.28	20.46	0.82	113.7	106.1	7.62	
Plat. I, Run 25.....	78.2	53.7	24.53	4.16	20.37	19.81	0.56	81.9	73.9	8.00	Cup 1, Alundum I + .0007
Plat. II, Run 25.....	25.23	17.1	9.10	0.73	8.37	8.24	0.13	30.44	29.0	1.46	Cup 2, Porcelain + 32 Alundum Coulometer I knocked down in washing.
Plat. I, Run 26.....	74.91	67.7	7.21	1.44	5.77	3.30	2.47	75.63	65.8	9.78	Alundum I + .0038
Plat. II, Run 26.....	48.57	33.0	15.59	1.82	13.77	13.29	0.48	56.50	52.7	3.82	Porcelain II + 56
Plat. II, Run 28.....	56.22	42.2	14.01	1.30	12.71	12.21	0.50	59.70	55.4	4.27	Porcelain 28 I/II + 0.062
Plat. I, Run 29.....	41.23	36.1	5.15	1.39	3.76	3.57	0.19	45.63	37.4	7.19	Alundum I + 0.061
Plat. II, Run 29.....	62.50	56.0	6.46	2.34	4.12	3.98	0.14	62.27	59.0	3.34	Porcelain II — 16
Plat. I, Run 30.....	64.89	55.7	9.20	3.31	5.89	5.56	0.33	66.62	61.3	5.31	Alundum I + 0.029
Plat. II, Run 30.....	27.13	21.1	6.05	2.52	3.53	3.28	0.25	32.14	29.7	3.39	Porcelain II 30
Plat. II, Run 33.....	89.00	86.6	20.40	1.37	16.25	.76	0.27	77.09	73.2	3.78	Anolyte, low, I 0
Plat. I, Run 33.....	72.06	58.9	13.11	.96	12.15	11.80	0.35	74.95	71.5	5.45	Catholyte, low, II 17 + 0.0143
Plat. I, Run 34.....	50.59	32.2	18.41	3.86	14.55	13.04	1.51	58.24	52.3	5.88	Catholyte, low, I + 0.0218
Plat. II, Run 34.....	62.29	48.1	14.22	2.61	11.61	11.18	0.43	66.45	63.2	3.28	Anolyte, low, II 5 + 0
Plat. I, Run 35.....	65.07	50.5	14.57	2.31	12.26	11.95	0.31	56.83	52.9	3.94	Anolyte, low, I
Plat. II, Run 35.....	79.34	63.8	15.52	2.30	13.22	12.69	0.53	74.74	71.7	3.01	Catholyte, low, II 13 + 0.0145 Catholyte, low, III + 0.0467
Rayleigh, Run 35.....	2.	128.7	. . .	. . .	. . .	. . .	. . .	. . .	. .	. . .	
Rayleigh, Run 20.....	174.6	143.3	31.30	6.43	24.87	21.86	3.01	135.0	123.1	11.93	
Kahlbaum, Run 20	184.2	111.3	72.28	15.48	56.80	55.18	1.62	138.8	103.3	35.52	

In runs 25 to 30 Mr. Buckner had in series the two platinum cups, with his purest silver nitrate solution in each. In one he used a porcelain cup to retain the anode slime, in the other an alundum cup which was quite porous and allowed the anolyte to mix with the catholyte. In every case except run 29 the silver from the coulometer with the alundum cup contains considerably more inclusions than the other. It seems very probable that the samples from run 29 were mislabeled. Calculating the gas condensed at —70° C. as water, the gas condensed between —70° and —180° C. as carbon dioxide, and the final residue of gas unoxidized or condensed as nitrogen derived from silver nitrate, and neglecting the others, we obtain the following results:

TABLE IV.

Deposit	Water per Gm. Deposit	Carbon Dioxide per Gm.	Silver Nitrate per Gm.
Run 25, porcelain	0.013 mg.	0.0016	0.0021 mg.
Run 25, alundum	0.044	0.0082	0.0084
Run 26, porcelain	0.037	0.0028	0.0072
Run 26, alundum	0.054	0.0035	0.0047
Run 28, porcelain	0.034	0.0026	0.0035
Run 29, porcelain	0.045	0.0046	0.0022
Alundum	0.030	0.0027	0.0023
Run 30, porcelain	0.046	0.0049	0.0049
Alundum	0.061	0.0064	0.0040
Average for porcelain ..	0.035	0.0033	0.0040
Average for alundum ..	0.047	0.0052	0.0049

The total difference in weight based upon these results is 0.015 mg. per gram, which would give a deposit in the coulometers with alundum cups heavier by 0.0015 percent. Mr. Buckner found a difference of 0.0025 percent, or, omitting the first result, which is very doubtful, 0.0032 percent. This is about twice the difference shown by the inclusion determinations. Above we have calculated the carbon dioxide as such. It does not seem credible that such a large amount of carbon dioxide could be included in the crystals, as there must have been very little in the electrolyte. It is a well-known fact that any colloidal substance is carried along by the current and deposited at the cathode. Rayleigh and Sedgwick showed that a very small amount of

silver acetate in the electrolyte had a very marked effect on the deposits, the losses on heating such deposits being much greater. We have repeated this experiment, and found that the silver from such a solution was very impure and liberated a very considerable quantity of carbon dioxide when dissolved in tin. It seems probable, therefore, that this carbon dioxide liberated from the silver deposits from supposedly pure silver nitrate represents some colloidal silver compound, possibly silver carbonate. If this is the case, instead of 0.0033 mg. of carbon dioxide we have 0.020 mg. silver carbonate. The difference between the weights of inclusions in the porcelain and alundum cups would then be correspondingly increased to 0.0025 percent.

In the last runs, 31 to 36, Mr. Buckner had in series the two platinum cups provided with porcelain porous cups and with his best silver nitrate solution as electrolyte in each. But the one was so arranged that diffusion of the anolyte into the catholyte took place, while in the other the diffusion was from the catholyte to the anolyte. Analyses of the deposits from runs 33, 34 and 35 have been made.

TABLE V.

Deposit	Water per Gram Silver Mg.	Carbon Dioxide per Gram Silver Mg.	Silver Nitrate per Gram Silver Mg.
Run 33:			
1. Catholyte into anolyte	0.046	0.0032	0.0051
2. Anolyte into catholyte	0.039	0.0075	0.0042
Run 34:			
1. Anolyte to catholyte..	0.027	0.0075	0.0220
2. Catholyte to anolyte..	0.038	0.0052	0.0068
Run 35:			
1. Catholyte to anolyte..	0.041	0.0043	0.0048
2. Anolyte to catholyte..	0.051	0.0045	0.0080

Averaging these results we obtain:

	Water	Carbon Dioxide	Silver Nitrate
Catholyte mixed with anolyte	0.046 ± 6	0.0065	0.0104
Catholyte free from anolyte	0.042	0.0042	0.0053

The total difference in the weight of inclusions in the silver deposited from the solution when the anolyte diffused into the catholyte and when it did not is 0.0114 mg. per gram of silver. This would correspond to a difference in the weight of the deposits of 0.0011 percent, which would be increased to 0.0023 percent if the carbon dioxide were calculated as silver carbonate. Mr. Buckner found that the deposits formed where the anolyte diffused into the catholyte were on the average 0.018 percent heavier than those formed under normal conditions when the catholyte was kept free from the anolyte. This difference is much greater than can possibly be explained on the basis of differences in inclusions, as far as our results show.

Hulett and Duschak concluded from their experiments that there was selective absorption of silver nitrate in the crystals. The average of their last eight determinations of deposits from normal solutions gives 0.038 mg. water and 0.0045 mg. silver nitrate per gram silver, or the weight of the silver nitrate is about 12 percent of the weight of water in the crystals. The electrolyte was a 15 percent solution, so there can be no question of adsorption of silver nitrate from pure solutions. There is considerable variation in the abnormal solutions, and they frequently show an excessive percentage of silver nitrate. This is particularly the case with the Rayleigh coulometer silver. In the Rayleigh deposit, in run 20, there was 0.058 mg. water per gram and 0.040 mg. silver nitrate. Here the weight of silver nitrate is 69 percent of the weight of water present. The silver nitrate in the Rayleigh coulometer is undoubtedly contaminated by colloidal organic matter from the filter paper. It is a well-known fact that organic colloids interfere with the regular crystallization of metallic deposits and such colloids are added to electrolytes for the purpose of obtaining smoother deposits and to prevent "treeing." It is also probable that the colloid in interfering with the normal crystallization of the electrically deposited silver also brings about a condition which favors increased inclusion and adsorption from the electrolyte, which accounts for the observations we have made and for the abnormal weights of silver obtained from impure silver nitrate solutions. There may be present in silver nitrate solutions which have been in contact with organic matter, colloidal silver compounds or

even some colloidal silver which may be imprisoned in the growing silver crystals, but this could hardly make a weighable difference in the mass of the deposit, the inclusion being largely silver nitrate and water.

The electrochemical equivalent of silver has been determined recently by Smith, Mather and Lowry on the assumption that the deposits in the silver coulometer were pure silver. Our results show that silver deposited from the purest silver nitrate solution kept free from filter paper or anode liquor contains at least 5 parts in 100,000 of impurity, and may contain several times this amount in deposits formed in the Rayleigh coulometer, which was the form used in their determinations. The figure given by Smith, Mather and Lowry for the electrochemical equivalent of silver is 1.11822 mg. per coulomb, but the last figure has no significance and the figure before the last is in question, due to the inclusions.

Princeton University.

DISCUSSION.

DR. GRINNELL JONES: Mr. Chairman, Professor T. W. Richards, who is unable to be present today, asked me to say a few words on his behalf in this discussion. Professor Richards agrees with Professor Hulett very strongly that the silver deposited on the coulometer does contain impurities, as proved by Lord Rayleigh and Mrs. Sedgwick long ago, and conclusively confirmed by Professor Richards. This point is of very great importance, in view of the fact that Smith, Mather and Lowry, who have made a very extensive investigation of the silver coulometer, ignore it, and Van Dyck denies it. So that we have here Professor Richards and Professor Hulett standing together in opposition to these foreign investigators on this point.

A paper presented at the XXII General Meeting of the American Electrochemical Society, in Joint Session with Sections II: Inorganic Chemistry, Xa: Electrochemistry, and Xb: Physical Chemistry, of the VIII International Congress of Applied Chemistry, in New York City, September 9, 1912. Dr. W. Lash Miller in the Chair.

STUDIES ON THE SILVER COULOMETER*

By G. D. Buckner and G. A. Hulett.

Introduction.

Previous to the starting of this investigation there had been extensive studies and experiments made with the silver coulometer, dating back to the fundamental work of Rayleigh and Sedgwick[1] in 1883, when the coulometer first became an accurate instrument for the measure of electric current. The present investigation was undertaken in order to throw light upon a matter which had received no attention in the numerous articles published on the silver coulometer.

In the discussion which followed Duschak and Hulett's[2] work on the silver coulometer the point was made by Mr. Hering[3] that, since platinum is known to contain oxygen in some form, it seems possible that dissolved oxygen may play some part in the deposition of silver, and it would naturally follow that abnormal weights might be caused thereby.

Platinum is known to take up oxygen either in solution or as a compound, forming an oxygen electrode in equilibrium with the oxygen in the electrolyte. On passing a current through a solution of silver nitrate the main reaction at the cathode would be the deposition of silver, but some of the current would go to the removing of the oxygen, and, since 8 grams of oxygen are equivalent to 107.88 grams of silver, it follows that there might be a deficit in the amount of silver deposited, an amount which might easily admit of measurement. It seemed possible that

* The work described in this article was made possible by a grant from the Elizabeth Thompson Science Fund, which placed at our disposal some of the special apparatus and materials needed for this investigation, and the authors take pleasure in acknowledging their indebtedness to the Trustees of the Fund.

[1] The literature of the coulometer is particularly reviewed by Guthe, Bull. No. 3, Bureau of Standards, 1905, page 347, and by Smith, Mather and Lowry. Phil. Trans., **207**, 545. Rayleigh and Sedgwick; Phil. Trans., **175**, 111 (1884).

[2] Duschak and Hulett: Trans. Am. Electrochem. Soc., **12**, 257 (1907).

[3] Hering: Trans. Am. Electrochem. Soc., **12**, 293 (1907); Bose: Chem. Ztg., **26**, 67 (1902).

information on this question could be obtained by using as a cathode cup some metal such as gold, which does not measurably absorb oxygen.

Considerable work has been done on the silver coulometer in vacuo and in solutions saturated with nitrogen, which means the exclusion of oxygen, and, while the evidence is not conclusive (most experimenters have observed a heavier deposit where oxygen has been excluded), this might be explained by the foregoing assumption.

The type of coulometer used by us was essentially the same as that used by Duschak and Hulett. Two of the cups were made of gold and two of platinum, each containing a porous cup to retain the heavy anode liquid. These were run in series, with the idea of comparing the silver deposited on platinum and on gold, in order to determine whether gold could be substituted for platinum as a cathode and thereby overcome the influence which might be caused by the oxygen in the platinum.

We soon found that the purity of the materials used in making up the electrolyte affected the deposits, and also that the inclusions in the deposited silver had to be taken into consideration, so this investigation really involved several important questions, and has resulted in two independent researches. Since it soon developed that the slight impurities in the electrolyte caused measurable variations in the weight of the silver deposited, it seemed probable that this variation in the weights might be due to the variation in the impurity included by the deposited silver. A very careful study of inclusions in electrolytic silver was taken up by Mr. J. S. Laird, and a method developed for the accurate determination of these inclusions, as described in a separate paper. Our first problem was to get a standard reproducible silver nitrate solution.

Incidentally we obtained some information from the suggestions of Richards[4] and others that a complex ion is formed at the anode, and that when this anolyte comes in contact with the cathode the deposit of silver is too heavy. In testing this point we arranged two coulometers in series, in which we maintained by the use of syphons the catholyte and anolyte at such levels that in each cathode cup the flow of the liquid would be towards the opposite pole.

[4] Richards, Collins and Heimrod: Proc. Am. Acad., **35**, 123 (1899).

We also attempted to substitute "Alundum" cups made of pure Al_2O_3 for the porous porcelain cups, since these permitted an easier flow of liquid and lessened the resistance.

In series with most of these experiments we ran a coulometer of the Rayleigh type, using the filter paper inclosed anode. We also experimented with electrolytes of different degrees of purity.

Apparatus Used.

Each cathode cup was 10 cm. high, 5 cm. in diameter, and weighed 72 grams. The cups were so adjusted as to weigh within 0.001 gram of each other, the advantage of this being that one tare would suffice for all of the cups and the exact differences in weight could be determined with the rider. The cathode cups Nos. *1* and *2* were of platinum, while *3* and *4* were of pure gold. These cathode cups were handled with tongs at all times. They were thoroughly cleaned with sea sand, also chemically, and washed, after which they were heated to redness for ten minutes in an electric furnace. This final treatment produced a surface on the gold cups to which the silver adhered so tenaciously that it could not be readily detached. Since the deposits were to be saved, this treatment was abandoned. When, however, the cathode cups were placed in wooden molds, and the internal surfaces made smooth with a blood-stone burnisher, then cleaned as stated above and heated in an electric furnace at 160° for thirty minutes, it was found that this treatment gave a gold surface from which the silver deposits could generally be removed with a platinum spatula. The deposits in the platinum cups could always be removed with ease.

The weighings were made under the same conditions as those described by Duschak and Hulett, the only difference being that the swing divisions were read through a small telescope fixed in the balance case. Duplicate weighings could be made to 0.02 mg. with certainty. Care was always taken that temperature equilibrium had been established in the balance case, and the cups were always placed on the pans with long tongs. The weights were calibrated, and at each weighing the temperature, barometer and hygrometer were noted. The anodes were made of "atomic-weight" silver, the purification of which is described elsewhere. The silver was melted in a porcelain cru-

cible and cast into cylindrical sticks 6 cm. by 1 cm. in a mold made of pure graphite which had previously been heated to redness for thirty minutes. These anodes were suspended by platinum wires which served as electrical connections. The four cathode cups were cleaned, adjusted to the same weight by removing a little from the top of the heavier ones, cleaned as described above, cooled in separate vacuum desiccators, and finally weighed.

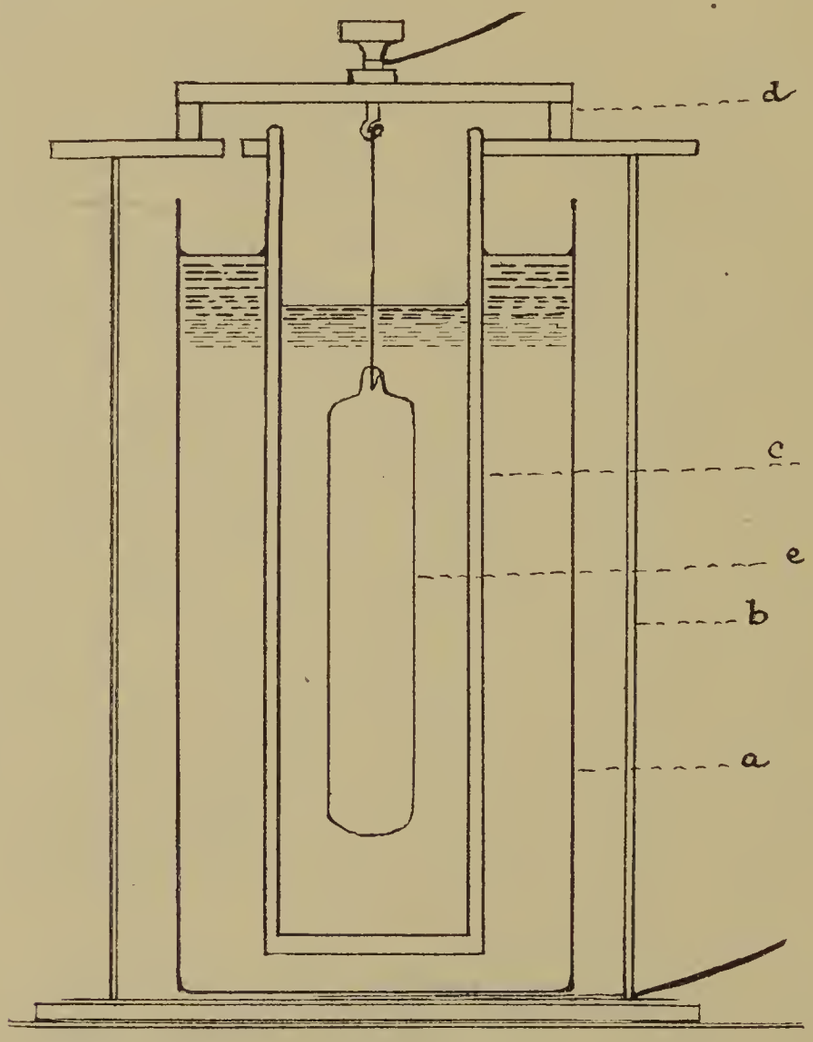

FIG. 1.

The cathode cups were now set up ready for a run, on circular pieces of plate glass the bottoms of which had been previously paraffined and on the top of which had been placed several pieces of filter paper to insure perfect insulation. The cathode cups *(a)* as shown in Fig. 1 were surrounded by glass jackets *(b)* which extended 2.5 cm. above the cups, and the glass cylinders were covered with pieces of glass provided with two holes, those in the center being just large enough to hold the porous cups *(c)*,

while those at the side and through which the catholyte was introduced were smaller. On the glass cover rested a hard rubber bridge *(d)* from which the anode *(e)* was suspended as indicated in the figure. In series with these four coulometers we ran one of the Rayleigh type, modeled after the specifications prepared by the National Academy of France. The Rayleigh bowl was 9 cm. by 4 cm. deep.

The porous cups were exact copies in size and texture of the Berlin "Pukel" filter tubes except that the upper 3 cm. were vitreous. They were 2.5 cm. in diameter by 12 cm. long, and when placed in position extended to within 0.75 cm. of the bottom of the cathode cups. These porous cups were treated with concentrated nitric acid, and then water was allowed to flow through them continuously until the last trace of nitric acid had been removed. At no time were they glowed or allowed to dry out. During a run the anolyte was removed at intervals with a constant level pipette and the catholyte added, so that the electrolyte was always flowing into the porous cups towards the anode. After an experiment had been completed the silver crystals were loosened with a platinum spatula and sealed in test tubes which had previously been glowed. This silver was examined by Mr. Laird, as described in another communication.

Materials Used.

In previous work we learned that filter paper was to be avoided, and in the present investigation we soon found that not only filter paper, but dust, organic matter of every kind and even dissolved glass so affected a silver nitrate solution that it gave abnormally heavy deposits. This research is therefore largely devoted to the question of the purity of the materials used in coulometer work.

In order to have a reliable and reproducible basis of comparison it was found necessary to work with a silver nitrate solution made in a definite way, which was essentially the same as that used by Richards in preparing the silver nitrate from which he determined the atomic weight of silver. This must give us a solution in which the equivalence between Ag and NO_3 is exactly equal, provided we rigorously exclude organic matter in all subsequent operations. We therefore paid particular attention to the elimination of all organic matter from our water, and

used only quartz, gold and platinum vessels, so that there could be no possible reduction of the silver nitrate by dissolved glass or by any other reducing agent. This is our "normal" coulometer electrolyte.

Preparation of Silver.

The first step in purifying silver is to obtain it in the form of silver chloride. Richards[5] digested silver chloride in a solution of potassium hydroxide and sugar, in order to obtain metallic silver. If, however, the silver chloride is dissolved in ammonium hydroxide and filtered, certain substances are eliminated, and there is an advantage in reducing silver directly from a solution rather than from the solid. We encountered a difficulty in reducing the silver from an ammoniacal solution with hydroxide and sugar in a desirable crystalline form, but found that this could be done as follows: Silver was obtained from the U. S. Mint, dissolved in nitric acid and precipitated as silver chloride. It was then digested in aqua regia for several hours on the water bath, filtered and washed. The silver chloride was dissolved nearly to saturation in a closed container in ammonium hydroxide of specific gravity 0.93. Five hundred c.c. of this silver-ammonium chloride solution was then decanted and filtered into a liter flask which contained 25 g. of cane sugar dissolved in 50 c.c. of water. Silver did not appear at first, but when the solution was heated to incipient boiling the silver began to separate in a very finely crystalline form. The ammonia which distilled was led into pure water for future use. As the reduction proceeded a solution containing 100 g. of sugar and 25 g. of potassium hydrate in 150 c.c. of water was added through a dropping funnel, rapidly at first and more slowly as the evolution of ammonia becomes less. After the sugar solution had been added and the evolution of ammonia had ceased, the liquid was vigorously boiled for fifteen minutes. Under these conditions we were able to reduce silver from an ammoniacal solution in a crystalline form which could be readily washed. It was found to be finely granular, and contained only exceptionally the slightest traces of silver chloride, which were entirely removed by shaking thoroughly with ammonium hydroxide. The small-grained silver possessed the virtue of lessening the possibility of

[5] Richards and Wells: Jour. Chem. Soc., 27, 475 (1905).

silver chloride and other impurities being occluded, it was easily soluble in nitric acid, and the solution gave no cloudiness on dilution. The silver was now placed in a Jena flask, dissolved in nitric acid, the solution evaporated, and the residue fused in an electric furnace. The fused silver nitrate was dissolved in "conductivity" water, and the metal precipitated with ammonium formate according to the directions of Richards and Wells. This silver was composed of large crystals, and was as pure as "atomic-weight" silver. It was melted and cast into molds, as has been already described. This silver was used in the preparation of our "normal" electrolyte.

Purification of Water.

Since dust, organic matter or dissolved glass in the water would partially reduce our purest silver nitrate, particular care was exercised in purifying the water employed in our work. The apparatus consisted of a 15-liter Jena retort, the neck of which was drawn down and cut off so as to just fit a quartz condenser tube ground into and *extending into the retort.* The arrangement was such that only vapor could enter the condenser, the water separating on the glass simply flowing back into the boiling liquid. Air filtered through absorbent cotton and deprived of all organic matter by passage over a glowing platinum spiral, wound evenly on a porcelain tube, was bubbled slowly through the gently boiling water. This water contained a small amount of $KMnO_4$ and $Ba(OH)_2$ and was freshly prepared conductivity water. The whole apparatus was drained for fifteen minutes before any water was condensed, only the second third being caught and retained in a quartz flask. Since this water had been in contact with quartz only, it must have been free from all traces of dust and organic matter.

Preparation of Silver Nitrate and Nitric Acid.

The nitric acid was purified according to a method identical in the main to the one employed in obtaining pure water. No air, however, was bubbled through the acid during its distillation. The purest silver was dissolved in this nitric acid and water prepared by the foregoing method. The quartz flask was placed in an electric furnace where the temperature was accurately con-

trolled, the solution was evaporated, and the residue fused according to Richards' directions until the last trace of nitric acid had been expelled. Extending down into the quartz flask which contained the silver nitrate was a porcelain tube through which passed air purified as previously described. The silver nitrate was kept covered, in a dark place, until used the day following, and the water was prepared and the solution made just before the experiment was started. A 15 percent solution was used in all experiments. We regarded this as the purest obtainable silver nitrate solution on a reproducible basis.

Manipulation.

After obtaining the accurate weights of the cathode cups they were placed on the circular glasses and filter papers with a strip of platinum foil under each cup, which served as a conductor for the electric current. The glass jackets were placed over them, and the silver nitrate solution, prepared as above, was added. The porous cups were now rinsed with silver nitrate solution and placed in position; thus the catholyte began immediately to diffuse into them. The anodes were fixed in place, and then the anolyte was added, but only to such a level that the catholyte was always passing into the anode chamber. After a current of about 0.3 ampere had passed through the coulometers for about four hours, depositing approximately 5 grams of silver in each cup, the current was broken and the anodes were removed. The anolyte was drawn off with a pipette, and following this the catholyte was removed by the same method. Finally the porous cups were removed and examined for small particles of loose silver which might have adhered to them. The anolyte and catholyte were reserved in separate flasks, and, although all solutions were tested for acidity, they were always found to be neutral.

The cathode cups were allowed to drain into small crystallizing dishes, each inclined against a glass support. The cups were next filled with distilled water, which was removed with a freshly-blown bulb pipette, run into a marked flask, and the cathode cups were drained again into the same crystallizing dishes. This was repeated three times, until the water which had stood over night in the cups gave no test for silver with KI. It was quite

impossible for any loose silver to escape us in this way, for previously it was shown that as little as 0.002 mg.[2] of silver could be detected in a flask and recovered. The cathode cups were always handled with tongs, wound with linen thread, so that no dust or liquids came in contact with the outside of the cups, which were always bright and polished. The loose silver was placed in the proper cathode cups, and these were dried in vacuum desiccators and weighed. We also satisfied ourselves that there was no appreciable change in weight when the cathode cups with the deposits were subsequently heated to 160° for thirty minutes. In the experiments made using the two platinum and two gold cathode cups a "Rayleigh" form was also run in the series. The results are as follows (Table I):

TABLE I.

Run No.	On Pt.		Differences mg.	On Au		Differences mg.
	1	2		3	4	
7	5.83369	5.83383	0.14	5.83449	5.83444	.05
8	5.47605	5.47586	0.19	lost	5.47637	....
9	5.59653	5.59663	0.10	5.59756	5.59746	.10
10	4.98000	4.97953	0.47	4.98036	4.98038	.02
11	6.26536	6.26540	0.04	6.26589	6.26603	.14

Run No.	Average Pt. deposit	Average Au deposit	'Rayleigh' deposit	Deposit on Gold heavier than on Pt. mg.	Rayleigh deposit heavier than on Pt. mg.
7	5.83376	5.83446	5.83525	+0.70	+1.49
8	5.47595	5.47637	5.47749	+0.42	+1.54
9	5.59658	5.59751	5.59848	+0.93	+1.90
10	4.97976	4.98037	4.98184	+0.61	+2.08
11	6.26538	6.26596	6.26661	+0.58	+1.23

If we calculate the percentage difference in the weight of silver deposited on platinum and on gold by the same current, we find that the deposits on the gold are 0.012 ± 0.0012 percent heavier than the deposits on platinum, while in the Rayleigh coulometer, where Kahlbaum's C. P. silver nitrate and the filter paper enclosed anode were used, we found the deposits to be 0.030 ± 0.0033 percent heavier than the deposits made on the normal platinum cathode cup. In every case it was found that the silver

deposited on gold was heavier than that deposited on platinum by the same current, the average excess being 12 parts in 100,000. This could be explained by assuming that part of the current in the platinum coulometers passed from the catholyte to the platinum cathode by removing oxygen from the platinum.

The silver samples reserved from these runs were investigated by Mr. Laird, but before the method of determining the conclusions was in its final state, the deposits from the gold cups showed in all cases slightly more inclusions and those from the Rayleigh form very much more than did the deposits from the platinum cups. The difference in the amounts of inclusions in the silver from the platinum and gold may be due to the fact that the silver crystals deposited on the gold were close together and nearly covered with gold, whereas those on the platinum were isolated.

These deposits on the platinum also contained impurities, so in our judgment it matters little which metal we use as cathode when the exact electrochemical equivalent of silver is to be determined, for the impurities in the silver deposit must be determined in any case if an accuracy greater than 1 in 5,000 is desired.

In examining the deposits we found that the silver crystals deposited on the platinum cathode were rather large and well defined, being placed irregularly on the sides of the cathode cups, with only a few on the bottom. Only in very few cases was there a tendency towards a striated arrangement of the crystals on the platinum, and in all cases the silver was easily detached by a platinum spatula without appreciably changing the weight of the cups. One of the difficulties encountered in using a platinum cathode was the fact that there was always a small amount of loose silver present which had to be recovered.

It seemed to us that gold might be a more desirable metal for the cathode cups than platinum, and when the surface of the gold cups was slightly rough there was generally no loose silver, but sometimes there was, for the adhesion of the silver crystals to the gold cups was not sufficient invariably to retain all of the silver during the manipulations. However, the adhesion was sufficient to make it a very difficult matter to remove the silver for examination as to inclusions. Gold is a soft metal, and the thin-walled cups were difficult to handle. Since the silver crystals

completely covered certain parts of the gold cathodes, and there may have been more chance for inclusions between the silver and gold than between the silver and platinum in the platinum cathodes, the platinum cups appear on the whole to be superior to those of gold, and if the dissolved oxygen plays any rôle it is only a few parts in 100,000.

The deposits in the "Rayleigh" form were feathery and striated at all times. The comparative character of the deposits in the platinum and gold cups can be seen in Fig. 2.

FIG. 2. The gold cup on the right shows the small Ag crystals as compared with those deposited on a platinum cup as shown on the left.

The Effect of Solutions of Known Purity.

Since the impurities in the deposits caused the abnormal weights, we decided to try some experiments in which the silver nitrate solutions in the cathode cups were of different but of known sources. In platinum cup No. *1* we used our "normal" solutions, in No. *2* a solution of Kahlbaum's C. P. silver nitrate which had been recrystallized after adding 1 c.c. of our purest nitric acid to the solution, decanting, evaporating and fusing the salt as directed above. The manipulation was carried out in detail as in the previous experiment. In the last four experiments we also ran a "Rayleigh" type which contained the same recrystallized silver nitrate solution contained in cup No. *2*. The results were as follows:

TABLE II.

Run No.	1 "Normal"	△ mg.	2 Kahlbaum's	mg. Heavier than Normal	Rayleigh Kahlbaum's
12	7.12175	0.58	7.12233	....	.....
13	4.96636	0.76	4.96560	....	.....
14	5.97746	0.82	5.97828	....	.....
15	5.86213	0.86	5.86299	....	.....
16	6.66193	0.29	6.66222	2.99	6.66492
17	5.72269	1.61	5.72430	3.19	5.72588
18	6.04101	0.41	6.04142	1.53	6.04254
19	5.04073	0.30	5.04103	3.18	5.04391
20	5.77169	—1.09	5.77060	2.09	5.77378

In experiment *20* the silver deposit in coulometer No. *2* was partially discolored, and, while the cause is unknown, it was obviously to be rejected, although we proceeded with the weighing as a matter of form. Referring to table No. *2*, coulometer No. *1* always contained our "normal" silver nitrate solution, while in No. *2*, which was like No. *1* in all other respects, was placed the solution made from our best water and Kahlbaum's silver nitrate, which had been treated with a little nitric acid, recrystallized and fused as previously described. This same solution was also used in the Rayleigh form. We expected to find that the Kahlbaum's C. P. silver nitrate when treated in this way would give the same results as our "normal" solution, but we found that coulometer No. *2* in every case gave a heavier deposit, the average excess being 0.009 percent. We noticed also that the Rayleigh form with the same solution as that in coulometer No. *2* gave a deposit which was always much heavier than that obtained from our normal electrolyte, the average excess being 0.036 percent. Furthermore, the deposits from coulometer No. *2* show distinctly more inclusions than those from coulometer No. *1*, while the deposits from the Rayleigh show still greater amounts of inclusions than from No. *2*.

It would follow, therefore, that the source and previous history of the silver nitrate solution always plays a measurable rôle in the weight of silver deposited by a given number of coulombs. We are therefore forced to the conclusion that it is necessary to determine and allow for the inclusions in the deposited silver when any attempt at great accuracy is made, and, although

reasonably pure materials for the electrolytes will suffice, the purer the solutions used the less the error due to inclusions, which is as small as one part in 10,000 for our "normal" electrolyte in a porous cup platinum coulometer, where the anolyte has no access to the catholyte during the electrolysis.

Effect Due to the Anolyte.

It has been maintained by Richards and others that the solution formed at the silver anode in a silver nitrate solution is abnormal in that it will yield an abnormally heavy deposit when used as catholyte. Table II clearly shows that the Rayleigh form gives a markedly heavier deposit than does the porous cup coulometer with the same solution. Filter paper has the property of so changing a silver nitrate solution that it gives a heavier deposit, a fact which in part or wholly would account for the difference between the results obtained with coulometer No. *2* and the Rayleigh form, as shown in Table II. There is another possible factor. In the Rayleigh coulometer the silver nitrate formed at the anode increases the density of the solution at the bowl, and it flows down through the filter paper and comes in contact with the cathode. In order to get some evidence on the possible effect of the anolyte we carried out the following experiments:

In our porous cup coulometers *1*, *2*, *3* and *4*, filter paper and all organic matter were excluded; furthermore, the anolytes in the porous cups were always maintained at a lower level than the catholytes, so that the flow of liquid was from the catholyte to the anolyte. Now, by keeping the electrolyte at a higher level in the anode than in the cathode cups, we can cause the anolyte to flow through the porous cups into the catholyte.

We ran two coulometers in series. From No. *1* we removed the anolyte by a constant level syphon which extended to the bottom of the porcelain cup, thereby removing the heaviest liquid as it collected at the bottom. In No. *2* the catholyte was removed by a quartz syphon which only extended below the top of the catholyte, thereby removing only the lighter and allowing the heavy liquid to flow through the porous cup and collect at the bottom of the cathode cup. The electrolytes were our "normal" silver nitrate solutions, and all details of the two coulometers

were identical except the direction of the flow of the electrolyte. The results were as follows:

TABLE III.

Run No.	Catholyte removed	Anolyte removed	Difference mg.
32	4.66181	4.66079	+1.02
33	4.13056	4.12998	+0.58
34	3.75443	3.75361	+0.82
35	5.12350	5.12286	+0.64
36	4.64026	4.63926	+1.00

These results show that the heavy anolyte does play some rôle in the formation of the heavier deposits obtained. These five results indicate an increase in weight of the silver deposited of 0.019 percent, due to the presence of the anolyte during electrolysis. This is approximately half of the increase in weight (0.036 percent) observed in the Rayleigh form, where the anolyte not only flows into the catholyte, but filter paper also is present.

Porous Cups of Different Material.

The porous cups with vitreous upper portion, which we used, were entirely satisfactory. They offered, however, more resistance to the current than was desired, and it took a considerable length of time to wash them absolutely free of acids. For other reasons it seemed desirable also to test porous cups made of some other material than porcelain, and we selected "alundum," which can be made into excellent filtering tubes. It did not seem conceivable that crystalline alumina could affect a silver nitrate solution. These tubes were of the same dimensions as the porous cups, only thin walled (1.5 mm.), allowed the liquid to filter through much more readily, and could be washed thoroughly in a short time. Four alundum cups having the above dimensions were obtained and thoroughly cleaned with nitric acid and water. Experiments 21, 22, 23 and 24 of Table IV were made with these substitutes for the porous porcelain cups, the normal electrolyte being used. The catholyte and anolyte were maintained at the same level. Here the agreement of the results obtained with the platinum cups No. *1* and *2* is particularly good, and a comparison

of the results obtained with the gold cups *3* and *4* is also good; but here again we find the heavier deposits in the gold cups. In run 23 there was a very fine scum floating on the catholyte in the platinum cups which could not be accounted for. The run, however, was completed as in all cases. These alundum cups retained the anode slime perfectly, but are quite porous, and no doubt some of the anolyte diffused through them to the catholyte. We therefore made six experiments with the two platinum cups. Coulometer No. *1* was provided with an alundum porous cup in which the anolyte was at the same level as that in the cathode chamber, while No. *2* contained the original porcelain cup where the anolyte was at a lower level and there was no diffusion in to the catholyte. In every case except in 27 the coulometer with the alundum cup showed a heavier deposit. The average is 0.026 percent. The results are as follows:

TABLE IV.

Run No.	1 Alundum	Difference mg.	2 Alundum	Gold heavier than Plat. mg.	3 Alundum	Difference mg.	4 Alundum
21	5.88568	0.31	5.88537	+2.06	5.88766	0.16	5.88750
22	5.33804	.05	5.33809	+0.59	5 33874	0.16	5.33858
23	5.71143	.05	5.71138	—0.49	5.71104	0.22	5.71082
24	4.42802	.03	4.42799	+0.26	4.42820	0.06	4.42826
			Porcel'n				
25	4.71515	+0.03	4.71518	.....	.....	....	.....
26	4.92720	+0.19	4.92706	.....	.....	....	.....
27	4.36494	—0.14	4.36508	.....	.....	....	.....
28	4.52397	+0.28	4.52369	.....	.....	....	.....
29	5.11922	+0.31	5.11891	.....	.....	....	.....
30	3.83131	+0.11	3.83120	.....	.....	....	.....

The effect here is, no doubt, due to the anolyte diffusing through the porous alundum cup, and, while we could arrange syphons to keep it slightly lower and cause the flow to be into the anolyte, the use of syphons makes the apparatus complicated and causes the failure of a larger percent of the experiments than occurs when the denser, less porous porcelain cups are employed, where it sufficed to remove a little of the anolyte with a small bulb pipette from time to time, which is a simple operation, and, besides, there was no diffusion through the cup. Alundum cups could be made of the same texture as the porcelain

cups, but then they would lose the advantage of being easily washed. Our porcelain cups with vitreous upper portions were distinctly superior to the "alundum" cups, and the coulometers as used were made for simplicity and exactness in manipulation, and were quite free from sources of accidental error.

General Summary.

1. It was found that the slightest traces of impurities, such as dust and organic matter, so affected a silver nitrate solution that it gave abnormally heavy deposits. Particular attention was paid to preparing a reproducible "normal electrolyte." It was necessary to take unusual precaution in preparing all materials, and we used only quartz, gold and platinum utensils.

2. In preparing "atomic-weight" silver the usual method was modified. We found the conditions under which silver could be precipitated from an ammoniacal solution of silver chloride in a crystalline condition, which is a distinct advantage over reducing solid silver chloride with sugar and caustic potash.

3. In preparing pure water, particular attention was paid to the exclusion of dust and organic matter of all kinds, even to the burning of volatile organic matter which might be present in the air that came in contact with the solutions used. Since the solubility of glass suffices to affect measurably a silver nitrate solution, the water employed in our work was only permitted to come in contact with quartz.

4. Silver nitrate was obtained from "atomic-weight" silver and pure nitric acid, the excess of acid being driven off at a definite temperature in an electric furnace, and with the exclusion of all organic matter. With this silver nitrate a solution was prepared which contained exact equivalents of Ag and NO_3. Kahlbaum's C. P. silver nitrate, recrystallized and fused, gave a deposit 0.009 percent heavier than that obtained with our normal electrolyte, and other solutions yielded distinctly heavier deposits.

5. Four porous-cup coulometers were run in series. The cathode cups in *1* and *2* were of platinum, while *3* and *4* were gold. They contained the same solutions and were treated in exactly the same manner. In every case we found the deposits on gold to be heavier than those on platinum, the average excess being 12 parts in 100,000.

6. In experiments with a "Rayleigh" form which contained Kahlbaum's C. P. silver nitrate solution, when run in series with our normal coulometer, the Rayleigh gave a deposit 0.036 percent heavy. The anode of the coulometer was wrapped in filter paper, and the anolyte diffused through to the cathode during electrolysis.

7. In our porous-cup coulometers the anolyte was always lower than the catholyte, and the former did not flow through except in special experiments, which showed that when the anolyte is allowed to pass through the porous cup and come into contact with the cathode a deposit heavier by 0.019 percent was obtained. This is nearly one-half of the abnormal effect caused by the heavy anode liquid and filter paper as shown in the Rayleigh form.

8. Experiments were made with thin-walled porous alumina cups substituted for the porcelain cups. The silver deposits made using the alundum cups show a heavier deposit in every case, due to the anolyte passing through to the catholyte during electrolysis.

Princeton University.

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THE ELECTROCHEMICAL EQUIVALENT OF CADMIUM.*

By J. S. Laird and G. A. Hulett.

Introduction.

Faraday's law, that a definite quantity of electricity is associated with one gram equivalent of any ion, is, as far as we know, strictly accurate, probably as accurate as the law of conservation of mass. There is evidence that not even as small a quantity of electricity as 10^{-16} coulomb passes from an electrolyte to an electrode without a corresponding chemical change taking place, as has been shown by Ostwald and Nernst[1] and by Helmholtz.[2]

Comparison of the masses of different ions liberated from solution by the passage of the same quantity of electricity would be, theoretically at least, the simplest and most direct method of comparing equivalent weights. Such a comparison has been made in but very few cases with any degree of accuracy, mainly on account of two difficulties:

First. The solution of a metal in contact with the metal often contains two or more kinds of cations, all of which assist in carrying the current from electrolyte to electrode. This is particularly troublesome in the case of a metal as, for example, copper which occurs in more than one stage of oxidation or with more than one valency.

Second. There is in most cases great difficulty in obtaining a deposit which is pure and capable of being freed from the electrolyte without loss or oxidation in washing.

These two difficulties have vitiated almost all attempts to determine equivalent weights of metals electrochemically. Cadmium,

* The work described in this article was made possible by a grant from the Elizabeth Thompson Science Fund, which placed at our disposal some of the special apparatus and materials needed for this investigation, and the authors take pleasure in acknowledging their indebtedness to the Trustees of this Fund.

[1] Ostwald and Nernst, Zeitsch. f. Phys. Chem., 3, 120.

[2] Helmholtz, Journ. Chem. Soc., 39, 277.

which occurs in only one stage of oxidation, is free from the first difficulty. Apparently the only attempts to determine its electrochemical equivalent directly are those of Hardin.[3] He electrolyzed in series solutions of the double cyanides of silver and potassium and of cadmium and potassium. The electrolyte was contained in a platinum dish which served as cathode. Insoluble platinum coils served as anodes. The metallic deposits were washed before breaking the circuit, dried, and weighed. The results obtained were not concordant, and out of the mass of results obtained he selected five which agreed with each other and with the value for the chemical equivalent which he obtained by other methods. The results selected gave 111.93 as the atomic weight of cadmium based on silver = 107.92. If the atomic weight of silver is taken as 107.88, this value becomes 111.89. This low value, differing as it does by 4 or 5 parts in 1,000 from the accepted value, may probably be attributed to two causes:

First. The solutions, even if neutral at first, would soon become acid at the insoluble anodes; hydrogen ions would assist in carrying the current, be liberated at the cathode, and hydrogen would be occluded in the deposit. As the overvoltage of hydrogen on cadmium is not large, about 0.48 volt, hydrogen might readily be liberated as such. Every milligram of hydrogen liberated would represent a deficiency of 56 milligrams of cadmium.

Second. Cadmium deposited in this way is always in a finely divided crystalline form; it is always more or less oxidized, and is somewhat soluble in water, especially if it contains dissolved oxygen. Such crystalline deposits also always contain included electrolyte.

In the present research these difficulties have been avoided by the use of a mercury cathode. Hulett and Perdue[4] have shown that the advantages in using a mercury cathode in the electrodeposition of metals are greatly enhanced by using it contained in a platinum cup plated with mercury so that the mercury wets the platinum. With this arrangement it is impossible for any of the electrolyte to creep beneath the mercury as it does when it is contained in a glass dish. Washing is much facilitated, as it is

[3] Hardin, Journ. Amer. Chem. Soc., **18**, 1016.

[4] Hulett and Perdue, Journ. Phys. Chem., **15**, 147.

merely a question of washing the upper surface, and the amalgam need not be agitated, so there is small chance of oxidation and no chance of small particles becoming separated from the amalgam and lost. The overvoltage of hydrogen on mercury is high, *viz.*, 0.78 volt, and hydrogen is almost insoluble in mercury or its amalgam. The cadmium being deposited in mercury, there is, of course, no possibility of inclusion of electrolyte. The solutions used were perfectly neutral and contained no cations except cadmium ions and the very small number of hydrogen ions due to hydrolysis of the cadmium sulphate. Contamination of the solution at the anode was prevented by the use of pure cadmium anodes, and, further, the anode liquor was kept separated from the cathode by means of a siphon.

Preparation of the Materials.

Anodes: Cadmium deposited electrolytically from pure cadmium sulphate solution at a low current density in a coherent crystalline form was washed, dried, and fused under re-sublimed ammonium chloride in hard glass tubes. The nugget thus obtained was carefully washed to free it from adhering flux, and fractionally distilled in a hard glass tube in a high vacuum, the first and last portions being rejected. The cadmium was allowed to solidify and cool in the evacuated tube. Anodes were prepared from this cadmium by cutting off suitable lengths with a clean chisel, splitting them, and welding the halves together on a piece of platinum wire which served to make contact. The cadmium was protected from contamination by the hammer or anvil by filter paper. The anodes were cleaned, etched with hydrochloric acid, rinsed in distilled water, and kept in a vacuum desiccator until required.

Cadmium Sulphate: About 10 kg. of Baker's analyzed cadmium sulphate was dissolved in distilled water to form a 25 percent solution. Hydrogen sulphide was passed into the solution until a considerable precipitate was formed. The solution was then heated on the water bath for several hours, and the precipitate, darkened by sulphides of mercury and iron, filtered off. This operation was repeated, the second precipitate being pure yellow. Most of the cadmium was then precipitated by purified hydrogen sulphide, the precipitate carefully washed, transferred

to a large flask, and decomposed with a sufficient quantity of pure nitric acid. The sulphur set free was filtered off, and sulphuric acid added in quantity somewhat in excess of that required to completely convert the nitrate to sulphate. The solution was evaporated on the water bath in a large porcelain dish, covered with a sheet of filter paper, until most of the cadmium sulphate had been deposited, leaving a small liquid residue containing the excess of sulphuric acid. This was decanted off, the deposit dissolved in distilled water, and again evaporated to dryness. It was finally heated until the excess sulphuric acid had been driven off and the residue was dry and powdery. The anhydrous cadmium sulphate so prepared was dissolved in "conductivity" water to form a saturated solution, and allowed to crystallize in shallow crystallizing dishes covered with filter paper. Cadmium sulphate crystallizes in large, well-defined crystals. The solutions, however, show persistent supersaturation, and, if allowed to crystallize spontaneously, come down usually as a very large number of tiny crystals, which, starting clear, usually become cloudy, very few large clear crystals being formed. It was found possible to avoid this difficulty by seeding the saturated solutions with a considerable number of the small clear crystals, the majority of which will grow rapidly and without becoming cloudy. In this way as much as 150 grams of water-clear crystals have been obtained from 500 c.c. of solution at one crystallization. The large clear crystals were picked out with a pair of bone-tipped forceps, rinsed with "conductivity" water, and centrifuged.

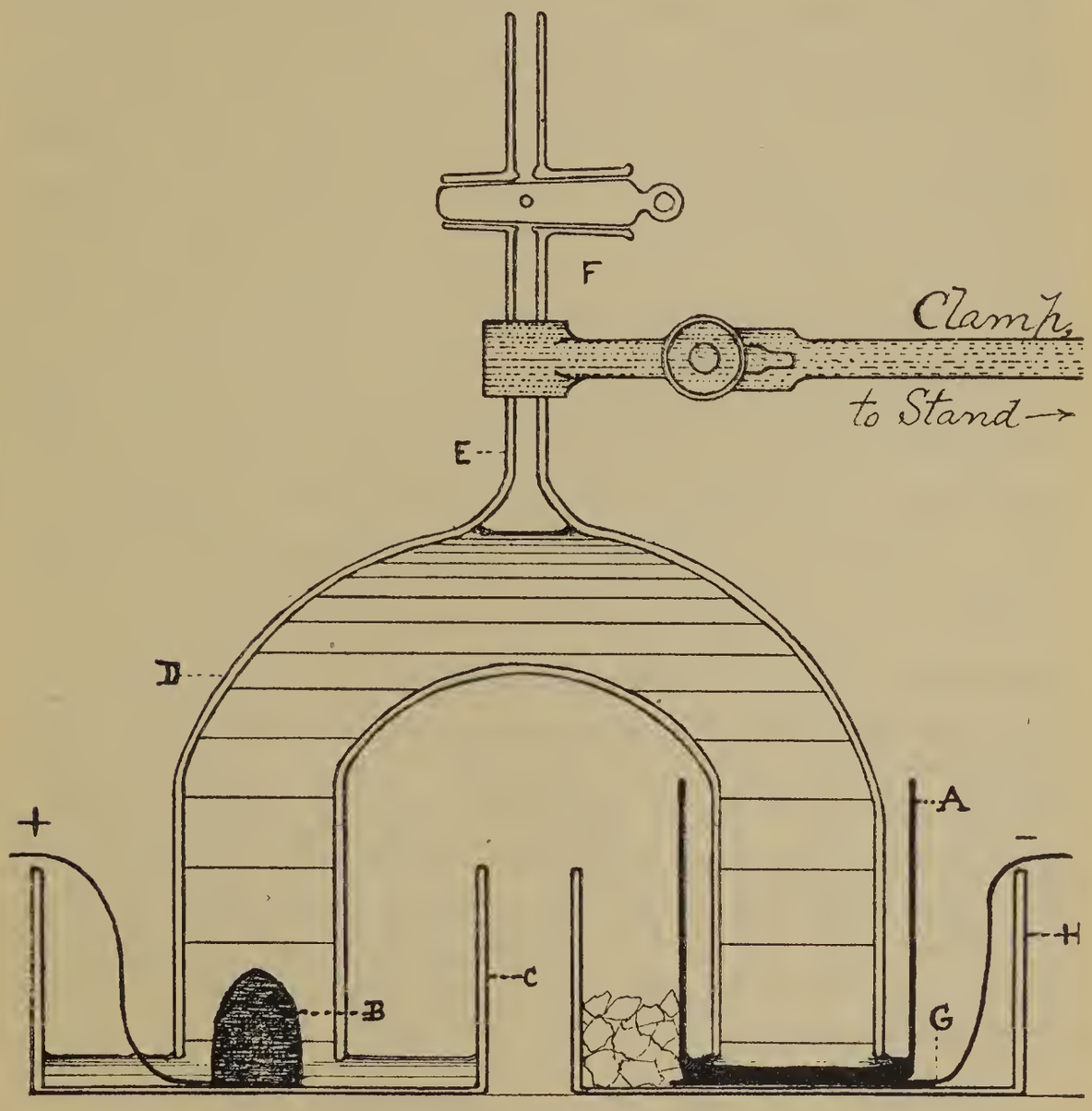
Nitric Acid: Baker's C. P. nitric acid was redistilled and condensed in quartz, the first and last portions being rejected.

Sulphuric Acid: Baker's C. P. sulphuric acid was redistilled under a pressure of 15 mm. and condensed in good Jena glass, the first and last portions being rejected.

Mercury: Mercury which has been shaken with dilute nitric acid was distilled three times in a slow stream of air under a pressure of 20 mm.

Water: Distilled water was allowed to boil gently in contact with potassium permanganate and barium hydroxide for twelve hours. It was then distilled and condensed in a block-tin con-

denser, the first fifteen liters being rejected. It was collected and stored in well-seasoned Jena flasks. That used in preparing the electrolyte or in washing the coulometers was freed from dissolved air by being gently boiled for several hours under a water-pump vacuum. It was delivered from a wash bottle under a slight pressure of hydrogen.



Apparatus.

The apparatus used in this research is shown in the accompanying diagram. Two special platinum cups, *A*, 5 cm. high and 4 cm. in diameter and weighing 40 gr. each, served as cathodes. They were carefully plated with mercury on the inside by heating mercury in them just to the boiling point. About 60 gr. of mercury was placed in each cup, a fresh supply being used with

each run. The anodes *B* were placed in small glass dishes *C*. A large glass siphon *D* provided with a suction tube *E* closed by a stop-cock *F* connected each anode dish with the corresponding platinum cup. This arrangement was resorted to in order to keep the cathode compartment as free as possible from anode liquor, because it had been found that the anode liquor acted very differently from pure cadmium sulphate solution. If it is allowed to come in contact with a bright deposit of metallic cadmium the deposit is blackened immediately, becoming covered with a layer of oxide. Also, if it is allowed to stand in contact with a cadmium amalgam the amalgam loses weight. The siphon was adjusted to within a millimeter of the mercury surface; thus, when the siphon was filled, the electrolyte stood just high enough above the level of the mercury to prevent the siphon emptying. No electrolyte being in contact with the walls of the platinum cup, the cadmium was necessarily deposited in the mercury. This arrangement gives a cell with a fairly high internal resistance even when a *2N* solution, which has a maximum conductivity, is used. To prevent the electrolyte from becoming heated by the passage of the current the cups were placed on platinum foil contacts *G* in small glass dishes *H*, which were kept filled with cracked ice. The vapor pressure of mercury at ordinary temperatures is quite small, only 0.001 mm., but it rises rapidly with rising temperature, being 0.01 mm. at 50° C. It was shown experimentally that mercury is volatilized from a mercury cathode during the course of an electrolysis lasting several hours if the electrolyte is allowed to become heated. By keeping the cups surrounded with ice this loss was avoided, and also the cold solution was found to give a perfectly bright mercury surface at the end of the run.

Conduct of an Experiment.

The electrolyte was prepared by dissolving 120 gr. of water-clear crystals of cadmium sulphate in 200 c.c. of air-free "conductivity" water. The coulometers were set up as described, in series with Mr. Buckner's silver coulometers, and electrolyzed with a current of 300 milliamperes for four hours. On breaking the circuit the siphons were allowed to empty and were removed. As much as possible of the electrolyte was removed with a

pipette and replaced by air-free "conductivity" water delivered under pressure of hydrogen from a wash bottle. This operation was repeated six times, the last two washings giving no test for cadmium with hydrogen sulphide. After the last wash water had been removed as completely as possible the outside of the cups was cleaned with pure filter paper, and they were placed in a vacuum desiccator which was quickly pumped out. The tops of the cups were covered with weighted pieces of filter paper to avoid any possible loss by spattering. The crucibles were allowed to dry over night, and then weighed to 0.1 mg. on a large Ruprecht balance, using the Borda substitution method and carefully calibrated platinum-plated weights. The vacuum correction for cadmium dissolved in mercury is —0.014 mg. per gram, and is therefore negligible on a weight of about 2 gr., being much less than the error of weighing in our experiments. The vacuum correction for mercury is —0 028 mg. per gram. This correction was applied, and there was also subtracted from the weights of silver found 0.06 mg. per gram, the average amount of inclusion found in the deposits.

Exactness of the Method.

The accuracy of the method was tested by blank experiments. After a run had been completed and the cup and amalgam weighed, the apparatus was set up and the electrolyte allowed to stand in the cups for two hours with no current passing through. The electrolyte was then removed, and the cups washed, dried and weighed exactly as in an experiment. The following results were obtained:

	Weight before	Weight after	Difference
No. 1.....	106.0620 gr.	106.0624	+0.4 mg.
No. 2.....	106.0619	106.0617	—0.2 mg.

The accuracy of manipulation is not quite as good as that attained by Hulett and Perdue[4] in their electrochemical determination of cadmium; for in our case it was not possible to keep the amalgam cathode during the removal of the electrolyte from the coulometers and their washing as they could with an electrolyte from which all the cadmium had been removed. Slight oxidation might have taken place which would make the

results too high, and small particles of the light oxide might have been swept away in the wash water and lost, making the results too low, but the blank tests show the errors to be not over one part in ten thousand.

RESULTS.

Run No.	Wt. of Cadmium	Wt. of Silver	Ratio Cd./Ag.	1/2 Cd++ Ag+ = 107.88
6	2.2721 2.2733	4.3638	0.52067 0.52095	56.170 56.200
7	2.3549 2.3534	4.5225	0.52071 0.52036	56.176 56.138
8	2.6637 2.6656	5.1186	0.52040 0.52077	56.140 56.179
9	1.9937 1.9938	3.8312	0.52039 0.52044	56.140 56.144
10	2.2979 2.2972	4.4148	0.52050 0.52034	56.151 56.134
11	2.4265 2.4261	4.6605	0.52065 0.52057	56.168 56.159
12	2.1496 2.1501	4.1297	0.52052 0.52064	56.154 56.167
14	2.6679 2.6675	5.1256	0.52051 0.52043	56.152 56.144

Mean ..... 56.157 ± 0.005

This series includes all the experiments which were brought to a satisfactory completion. Of the four results which have been excluded, runs 13 and 15, in one pair the siphons emptied during the run, causing mixing of the anode and cathode liquids, and consequently low results. In the other pair a drop of mercury was carried from one cup to the other in washing, and on account of this inaccuracy in manipulation they were excluded. They were weighed as a matter of curiosity, and the average of

the two came out to be 56.14, which is not far from the general mean.

Taking all the runs which were completed, the mean value of the electrochemical equivalent of cadmium is 56.157 for 16 determinations. The probable error of a single determination is ±0.012, while the probable error of the arithmetical mean is ±0.005 The probable error of a single experiment, one part in five thousand, is very nearly the error in a weight of two grams caused by the errors of manipulation, as indicated by the blank experiment. In run 6 the electrolyte became warm during the electrolysis, and there was considerable oxidation. The variation from the mean in these two determinations is 3 or 5 times as great as the probable error of a single experiment. They should therefore be given less weight in the result.

These results give 112.31 ± 0.01 as the atomic weight of cadmium, which is in very good agreement with the lower value recently proposed by Hulett and Perdue,[4] *viz.*, 112.30. It may be noted that such a degree of accuracy has not previously been attained with any form of coulometer except the silver coulometer using silver nitrate as electrolyte. It is proposed to continue this work using other solutions, as, for example, cadmium nitrate solution, which behaves better than the sulphate. It should also be possible to extend this work to take in other metals soluble in mercury, such as zinc, and thus obtain a direct comparison of their atomic weights with that of silver.

DISCUSSION.

A MEMBER: I should like to ask Mr. Hulett whether there was any danger of loss of cadmium in washing after electrolysis, because that would produce a lower result.

PROF. G. A. HULETT: Of course that is a point that we looked into very carefully. The details will be published, but I cannot give them here. We use, in washing, distilled water that was saturated with hydrogen, and we endeavor to keep all oxidizing solutions away from the amalgams. The presence of the mi-

nutest trace of oxidation becomes apparent as a tarnish on the surface of the mercury. One can readily detect an amount of oxidation which represents practically nothing as far as weighing is concerned. With the precautions we took, our amalgams remained quite bright. Then we had a check or blank experiment on this question. After we weighed our cadmium amalgam we put the solution back on the amalgam and then repeated all the manipulation of washing and reweighing and got results which indicated that our method was reliable to one part in ten thousand.

PROF. J. W. RICHARDS: Mr. Chairman, I just want to refer to the remark that Prof. Hulett made that inclusions were absolutely excluded in using mercury. My experience in handling mercury in a number of cases has been that it apparently gets wet inside somewhere in the body of it. There are a number of indications that the mercury is not absolutely free from some contamination by the solution with which it is in contact.

PROF. HULETT: We came to the conclusion that liquids were likely to be imprisoned in the mercury in the first part of our work, but we had some later experiences which rather proved that this was not true.

We attempted to dry our amalgams or mercury in a vacuum desiccator over calcium chloride, but found that the mercury spurted just as if it contained inclosed liquids. This was always observed when we used glass containers for the mercury or amalgams, but when we used amalgamated platinum cups for the mercury or amalgam there was no spurting on drying in the vacuum desiccator, so we concluded that the trouble was due entirely to the film of water which gets between the glass and mercury, but is entirely absent in an amalgamated platinum container. Possibly the film between mercury and a glass container would account for the observations of Professor Richards.

PROF. E. P. SCHOCH: I should like to ask Prof. Hulett if he will indicate to us the range of current densities, and whether there is a variation of this error with the current densities, since that might indicate whether the difference between the electrochemical equivalent, as Dr. Hulett found, and the atomic weight might not be due to the discharge from a high valent to a lower

valent ion without any deposition taking place, which, of course, would certainly vary with the current densities.

PROF. HULETT: I take it that Prof. Schoch's point is that if the current density is higher the inclusion would be more.

PROF. SCHOCH: Not inclusions, no. I mean the discharge from the bivalent to a lower valent ion—for instance, to monovalent cadmium, the existence of which has been demonstrated by T. W. Richards and his students. The portion of the discharge which would take place in this manner would not deposit any metal, and that would account for the lower chemical equivalent. Let us see—or does it work the other way?

PROF. HULETT: It works the other way.

PROF. SCHOCH: Upon reflection, it does not work the other way, and it may account for the discrepancy.

DR. G. S. FORBES: May I ask whether it would be possible for hydrogen at low pressure to be discharged, and to diffuse away from the mercury through the solution, as is the case with the residual currents where no bubbles of gas at all appear. Is it not possible that a small portion of the current may have been used in depositing hydrogen, which did not appear as bubbles, but diffused away and thus caused too little cadmium to be deposited?

The potential difference at the mercury cathode must be fairly high and it would seem that some such effect must come into the question.

PROF. HULETT: We have considered that point, and it is a point that is to be considered. I might say, however, that we have found no experimental evidence to substantiate such an effect; furthermore there are several things which favor the non-existence of the liberation of a measurable quantity of hydrogen with the cadmium. In the first place the decomposition potential of cadmium on mercury is very low. We have reduced very much the decomposition potential of cadmium on account of the solubility of cadmium in mercury. In the second place, there is a very considerable over-voltage as far as hydrogen is concerned. We have made it increasingly difficult for hydrogen to be deposited while we have the potential difference for cad-

mium at the mercury cathode very low. So I question whether there is any effect on our measurements so far as the liberation of hydrogen is concerned. The whole inquiry depends, so far as interpreting our results is concerned, on the atomic weight of cadmium.

Dr. W. Lash Miller: That is not known with any great accuracy, is it?

Prof. Hulett: I do not know. We have obtained from cadmium sulphate a figure which leads us to suspect that the atomic weight is 112.3 instead of 112.4 as given in the atomic weight tables. We are making analyses of cadmium chloride, which is anhydrous, by the same method, and we hope to get pretty definite information on this point.

A paper presented at a Joint Meeting of the American Electrochemical Society and Sections "Electrochemistry," "Physical Chemistry" and "Inorganic Chemistry" of the VIII International Congress of Applied Chemistry, in New York City, September 9, 1912. President W. Lash Miller in the Chair.

THE IODINE COULOMETER AND THE VALUE OF THE FARADAY.

By Edward W. Washburn and Stuart J. Bates.

PART I.

Review of Previous Coulometer Investigations.

1. *Introduction.*

Although Faraday's law of electrochemical change has been universally accepted for many years, there still exists a considerable degree of uncertainty regarding the exact numerical value of the Faraday. Theoretically, any chemical reaction which can be brought about by means of the electric current might be employed for the determination of the value of the Faraday, but as a matter of fact very few reactions have been studied in this connection, and the value at present accepted for this constant is practically based upon measurements with a single electrochemical reaction—the deposition of silver from an aqueous solution of one of its salts. In view of the amount of care and labor expended and the variety of reactions which it is deemed necessary to employ in order to fix the atomic weight of a single element, it is certainly remarkable that in the case of such an important and universal constant as the Faraday, scarcely any serious consideration has ever been given to any electrochemical reaction except that which occurs in the silver coulometer. And when we add to this the fact that this particular reaction is known to be affected by numerous sources of error and uncertainty which have not been entirely removed by years of laborious investigation, participated in by many chemists and physicists,[1] it must be apparent to all that serious consideration should be directed to the problem of discovering some other

[1] More than forty articles upon the silver coulometer are to be found in the literature of the subject.

electrochemical reaction which will fulfill the exacting requirements necessary for a successful determination of the Faraday at least as well and preferably more perfectly than does the process which occurs within the silver coulometer.

In addition to the silver coulometer, the copper, the iodine, and the "knall-gas" coulometers have received some attention from investigators, but none of them seems to have been considered seriously by the scientific world, either as a rival to or even as a valuable check upon the silver coulometer. Before taking up the description of the work of the present investigation it will be advantageous to review the results of previous investigations with the above coulometers[2] and especially the present state of affairs with reference to the silver coulometer.

2. *The Silver Coulometer.*

The large amount of study which this has received from so many investigators naturally arose from the fact that the international ampere is at present defined in terms of the mass of silver deposited per second from a solution of silver nitrate, under more or less definite physical and chemical conditions. The silver coulometer is apparently the only one receiving serious consideration at the present time, being in fact within the last five years the subject of extensive investigation by the national laboratories of the leading nations of the world. Of these investigations the following have been completed: (1) that of Smith, Mather and Lowry[3] at the National Laboratory of England; (2) that of Laporte and de la Gorce[4] at the Laboratoire Centrale d'Electricité, in France; (3) that of Jaeger and von Steinwehr,[5] at the Physikalisch-Technische Reichsanstalt of Germany; and (4) that of Rosa, Vinal and McDaniel,[6] at the National Bureau of Standards at Washington.

These investigations, together with that of Duschak and

[2] The lead and the mercury coulometers have also been studied to some extent, but will not be considered in the present discussion, as an accuracy greater than 0.1 percent is not claimed for them. See Mathers and German, Ind. Univ. Studies, 8, 41 (1910); Betts and Kern, Trans. Amer. Electrochem. Soc., 6, 67 (1904); Wright, Lond. Electrician, 60, 297, 319.

[3] Phil. Trans. A. 207, 545 (1908).

[4] Bull. Soc. Internat. Electriciens II, 10, 157 (1910).

[5] Z. Instrumentenkunde, 28, 327, 353 (1908).

[6] This work has not been published *in extenso,* but the final result is stated in the paper of Rosa, Dorsey and Miller, Bull. Bureau Stands., 8, No. 2, 367 (1911).

Hulett,[7] and that of Foerster and Eisenreich,[8] have added considerably to our knowledge of the behavior of the silver coulometer under various conditions. Foerster[8] has reviewed at length the work on this coulometer up to the end of 1909, and Professor Hulett has announced a paper upon the subject, to be presented to this Congress. It would, therefore, be superfluous to attempt anything like an exhaustive discussion of this coulometer in the present paper. In order to understand some of the results obtained in this investigation, however, it will be necessary to review briefly the present state of our knowledge respecting several of the factors which influence the accuracy and precision of the silver coulometer.

The Influence of the Anode Products.—The careful investigations of Smith, Mather and Lowry have shown that the difference heretofore observed between the filter-paper type of coulometer and the porous-cup type can be eliminated by using very pure nitrate and by employing a large bulk of solution, with the filter paper arranged in the form of a cup around the anode. Their conclusion upon this point has been confirmed by the results obtained by the German and the French investigators.

Smith, Mather and Lowry found as a mean of all their results, the value 1.11827 milligrams per coulomb for the electrochemical equivalent of silver. Laporte and de la Gorce obtained the value 1.11829. Jaeger and von Steinwehr's investigation was a comparison of the silver coulometer with the Weston cell and the International Ohm. If we adopt the value 1.01820 for the E.M.F. of the Weston normal cell, their results give the value 1.11815 for the electrochemical equivalent of silver. The American observers found the value 1.11804, using only porous-cup and non-septum types of coulometers.

The results obtained by the English and French investigators justify the conclusion that with sufficiently pure silver nitrate the errors due to the products formed at the anode may be eliminated equally well either by using a sufficiently large volume of solution *or* by placing the anode in a clean porous-cup. Whether the error from this source is entirely eliminated (or compensated) by *either* procedure is as yet rather uncertain.

[7] Trans. Amer. Electrochem. Soc., **12**, 257 (1907).
[8] Z. Physik. Chem., **76**, 643 (1911).

In fact some experiments of Eisenreich[9] suggest the possibility that *neither* type is perfectly efficient in preventing the anode products from reaching the cathode. Eisenreich found that both the filter-paper and the porous-cup coulometers gave too high results at 90°, the latter type giving deposits too high by as much as 0.1 percent at this temperature. Hence it is not impossible that the deposits obtained at ordinary temperatures may still be slightly but appreciably too great, owing to the diffusion of some of the anode solution through the porous-cup during the electrolysis. The evidence offered[10] by Smith, Mather and Lowry indicates, however, that in their experiments the error from this source is probably less than 0.003 percent.

The Purity of the Silver Deposit:—If the silver deposit after drying to constant weight still contains water or silver nitrate it should undergo a loss in weight on heating to sufficiently high temperature. Various estimations of this loss in different cases show such poor agreement that the amount and character of the included material is evidently subject to considerable variation with the conditions. Rayleigh and Sedgwick[11] found that well-washed deposits showed a loss of 0.01 to 0.02 percent on heating to the verge of redness. Richards and Heimrod,[12] dried their deposits to constant weight at 160° and then heated them over an alcohol flame to the verge of fusion. In twelve experiments the loss of weight varied from 0.003 to 0.030 percent., the mean value being 0.018 ± 0.002[13] per cent. Van Dijk[14] found that after washing and drying the deposit at 150° there was no further loss of weight on reheating to 500°-600°. Smith, Mather and Lowry heated their silver deposits to constant weight at 160°, and in eight instances they were afterward heated to 240° and in three to 400°, without any loss in weight being observed. Laporte and de la Gorce apparently did not heat their deposits above 160° in any instance. In six instances

[9] *l. c.*, page 680.

[10] *l. c.*, page 566.

[11] Phil. Trans., **175**, 411 (1884).

[12] Proc. Amer. Acad., **37**, 435 (1902).

[13] Throughout this discussion, unless otherwise stated, the quantity, $\frac{d}{\sqrt{n}}$ where d is the average deviation of the individual observations from the mean, and n is the number of observations, will be employed as the precision measure of the observed quantity.

[14] Arch. neerl., **10**, 287 (1905).

after drying the deposit at 160°-200°, Jaeger and von Steinwehr heated it to the verge of redness (not higher) and observed no loss in weight.

Both the English and the German investigators conclude that appreciable amounts of included material are not present in the silver deposit. This conclusion has been justly criticized by Richards[15], who points out that the temperatures employed were not sufficient to soften the silver and release the included material. The admirable experiments of Duschak and Hulett[7] upon this point have demonstrated beyond question that the silver deposit contains *both* water and silver nitrate, and that these impurities cannot be *completely* removed without fusion. In their experiments the total quantity of included material amounted to 0.014 percent of the deposit, for deposits in air, and 0.0084 percent for deposits *in vacuo*. These results are for a coulometer of the porous-cup type. The amount of this inclusion doubtless varies considerably with the type of the coulometer and the conditions of the experiment and should therefore be determined for each experiment (a tedious procedure) if an accuracy of 0.001 percent is aimed at. The value 1.11827 may therefore be in error from this cause at least 0.01 percent and possibly more, as the amount of inclusions in the deposits of Smith, Mather and Lowry is not known.

The Effect of Filter Paper.—Smith, Mather and Lowry do not seem to have made any direct experiments to determine whether or not the mere presence of filter paper in the silver nitrate solution produced any appreciable influence upon the deposit. Laporte and de la Gorce sought to answer this question by employing in one coulometer double the quantity of filter paper ordinarily used. In one experiment the coulometer with the double filter paper gave a deposit only 0.001 percent heavier than their ordinary coulometer, but in a second experiment the difference amounted to 0.012 percent in the same direction. A third experiment was made using a filter paper which had been previously soaked in the silver nitrate solution for seven hours and then washed and dried before using. The coulometer in which this paper was employed gave a deposit 0.005 percent lighter than their ordinary paper coulometer. These three experiments all point to an

[15] Proc. Amer. Acad., 44, 91 (1908).

appreciable, though small influence of the filter paper upon the mass of the deposit. This conclusion is substantiated by recent work at the National Bureau of Standards, where the use of two or three thicknesses of filter paper was found to materially increase the weight of the silver deposit.[16] This effect is ascribed to the presence of oxy-cellulose on the surface of the filter paper, which reduces silver nitrate to colloidal silver. This colloidal silver is then carried to the cathode where it is deposited, and by breaking up the crystalline silver, causes a greater inclusion of solution than would otherwise be the case.[17]

The Effect of Oxygen.—Smith, Mather and Lowry found that their coulometer gave the same result *in vacuo* as in air. Jaeger and von Steinwehr employed atmospheres of nitrogen and of hydrogen respectively, in different experiments, but the mass of silver obtained under these conditions was not appreciably different from that obtained in contact with the atmosphere.

In direct contradiction to these results, experiments of Duschak and Hulett show that the deposit from a water solution of pure silver nitrate, free from air and *in vacuo,* is distinctly *lighter* (nearly 0.01 percent in some cases) than one formed in air. This fact, supported as it is by two quite different but concordant pieces of evidence, namely, the directly determined difference in the mass of the deposits and their impurity content, seems indisputable. Results further indicate that saturating the solution with nitrogen produces the same effect as simply removing the air. The evidence upon this question seems, therefore, to be contradictory, and further investigation is needed.[18]

Summary.—The result of the above considerations may be summed up as follows: If very pure materials are employed, the results of the silver coulometer in the hands of a careful and experienced worker are reproducible to one or two thousandths

[16] Vinal, Science, N. S., **34**, 31 (1911).

[17] McDaniel, Science, N. S., **34**, 160 (1911).

[18] Foerster suggests that the results of Duschak and Hulett may be due to a diffusion of some of the anode solution through the porous cup during the five hours' time consumed in the electrolysis. This seems rather improbable, however, since the surface of the solution within the porous cup was kept one centimeter lower than that of the solution outside. Moreover, as Duschak and Hulett point out, the nature and amount of the included material was decidedly different in the two cases. Foerster's suggestion may, however, possibly explain the difference of "0.002 to 0.003 percent, unaccounted for," which Duschak and Hulett found between the masses of their deposits in the two cases (*l. c.,* page 291).

of one percent under a given set of conditions. The mass of the deposit even under the most favorable condition does not, however, correspond exactly to the reaction,

$$Ag^{+} + (-) = Ag,$$

but is greater than this reaction requires, owing chiefly to the inclusion of solution. The above considerations indicate that a *minimum value for the faraday* can be obtained from the silver coulometer operated under the following conditions:

(1) A large volume of solution of very pure silver nitrate free from dissolved oxygen; (2) An electroplated anode surrounded preferably by *two* perfectly clean porous-cups provided with suitable syphons for maintaining the proper level; (3) Electrolysis *in vacuo;* (4) Determination of and correction for included material by the method of Duschak and Hulett. Up to the present time no investigation in which all of these conditions have been simultaneously observed has been published.[19]

The value of the faraday which is generally accepted at the present time as that calculated from the work of Smith, Mather and Lowry, that is,

$$F = \frac{107.880}{1.11827} = 96{,}470 \text{ coulombs.}$$

For the reason stated above it seems probable that this number is too small by at least 0.01 percent, and possibly by as much as 0.03 percent, as every one of the four factors discussed above tend to produce too heavy a deposit.

3. *The Copper Coulometer.*

The copper coulometer has been the subject of a number of investigations. The work of Richards, Collins and Heimrod[20] may be considered as superseding that of earlier investigators. They found that the two most important sources of error influenced the result in opposite directions. (1) "Metallic copper slowly dissolves in an acid solution of cupric sulphate. * *

[19] The value 1.11804 obtained by Rosa, Vinal and McDaniel gives 96,500 coulombs as the value of the faraday, a result higher by 0.03 percent than that of the English observers. In a private communication to one of us, Dr. Rosa states that no determination of, or correction for included material was made in these experiments. Hence it is possible that their value, 1.11804, is still too large.

[20] Proc. Am. Acad., **35**, 123 (1899).

The losses of weight of the plates were found to be proportional to their respective areas, if the volume of solution was large." (2) "Plates of copper immersed in *neutral* solutions of cupric sulphate always *gain* in weight, becoming coated with a film of cuprous oxide."

The second source of error was eliminated by using a slightly-acid solution, while the influence of the former was reduced by employing a low temperature and working in an atmosphere of hydrogen. Assuming then that the rate of solution of the metallic copper varies directly as the area of the plate, it was possible by using plates of different areas as cathodes, in two coulometers in series, to extrapolate to the increase in weight of a plate of zero area, *i. e.*, to calculate what would have been the gain in weight of the cathode if none of it had dissolved.

A series of seventeen experiments was made with two copper coulometers having different sized plates in series with two silver coulometers of the Rayleigh filter-paper type. In each experiment the mass of copper was corrected to correspond to a plate of zero area as explained above. In most of the cases recorded the larger plate always showed the smaller deposit of copper, so that the "corrected copper" was larger than the amount deposited upon either plate. In three experiments, however (Nos. 9, 10 and 11), the larger plate showed the greater deposit, so that the "corrected" value was smaller than either of the observed values. These irregularities decrease somewhat the reliance which can be placed upon the results of the copper coulometer. The mean value for the atomic weight of copper obtained from this series of experiments was 63.563 ± 0.0044, a precision of 0.0069 percent.[21]

In order to correct this value for the errors in the Rayleigh filter-paper coulometer, Richards and Heimrod made a series of 18 experiments in which their filter paper coulometers were

[21] This precision measure is not from the original paper, but has been computed as explained in foot-note (13) of this paper. In a private communication, Professor T. W. Richards, to whom this portion of the manuscript was submitted, informs us that Collins' note-book contains an entry indicating that the copper solution employed in experiments 9, 10 and 11, referred to above, was slightly impure, without stating the nature of the impurity, which must, however, have caused the solutions to be somewhat basic, and hence to produce the abnormally heavy deposits obtained in these experiments. If, however, the results of these three experiments be rejected, practically the same mean value (65.564) is obtained as when they are included. The average deviation from the mean is 0.025 percent, and the maximum 0.081 percent, which shows that even under the best conditions the copper coulometer does not give very reproducible results.

compared with the porous-cup type and were found to give on the average a deposit 0.041 ± 0.0040[13] percent heavier than that of the latter type. In addition to this correction, a correction for included material (0.018 ± 0.0019 percent[22]) was also made which brought the value for the atomic weight of copper up to 63.601. This would have a precision of

$$\sqrt{(0.0069)^2 + (0.0040)^2 + (0.0019)^2}$$

or 0.0082 percent. This value is based upon the value 107.93 for silver. Assuming 107.88 for silver, we obtain finally the atomic weight 63.572 ± 0.0052 for copper, which is in very close agreement with the value 63.575 obtained by chemical means. If the assumption were justified that the mean value of the "corrected" copper obtained by Richards, Collins and Heimrod, represented only the reaction,

$$Cu^{++} + 2\,(-) = Cu,$$

then we would be justified in concluding that the "corrected" silver deposit obtained in the Richards porous-cup coulometer could be relied upon to give the value of the Faraday with an accuracy of 0.008 percent. In view, however, of the rather irregular behavior of the copper coulometer already referred to,[21] it is on the whole of rather doubtful value as a check on the silver coulometer.

Richards, Collins and Heimrod make the statement[23] that, "The last six determinations were consecutive; and in these the conditions of experiment were much more satisfactory than in the earlier ones; for much practice was naturally acquired in the course of the work." If we consider only the results obtained in these six experiments, we obtain for the atomic weight of copper the value, 63.575 ± 0.011. It seems, therefore, certainly safe to conclude that the silver deposit from the porous-cup coulometer of Richards cannot be in error by more than 0.02 percent, if correction is applied for included materials.

[22] See foot-note (13).
[23] *l. c.*, page 134.

4. *The Iodine Coulometer.*

The iodine coulometer has been studied by a number of investigators,[24] but for the present purpose the results of Kreider and Gallo alone need be considered; the earlier investigators did not claim an accuracy greater than 0.5 percent.

In Kreider's coulometer the cathode was surrounded with a solution of hydrochloric acid and the platinum anode with a solution of potassium iodide. The iodine formed at the anode was titrated with sodium thiosulphate. The amount of iodine liberated in two or three coulometers in series agreed within 0.01 or 0.02 percent. In *two* experiments the iodine coulometer was compared with a silver coulometer of the filter-paper type and the iodine liberated was stated to be from 0.06 to 0.09 percent *more* than that calculated from the silver coulometer. The atomic weights which were employed in this calculation are not given, neither are there any data from which they may be inferred. The atomic weights for 1904 were Ag = 107.93, I = 126.85; for 1905, Ag = 107.93, I = 126.97. The paper is dated June 1905, hence it is quite possible that the atomic weights for 1904 were employed. If this is the case, the amount of iodine formed, calculated on the basis of the atomic weights for 1912, is from 0.01 to 0.04 percent *less* than that which corresponded to the silver deposited. This is in agreement with the well-known fact that the Rayleigh filter paper coulometer gives too heavy a deposit of silver. Kreider's experiments were too few to justify any further conclusion from his results.

Gallo's investigation was undertaken in the hope that the results might throw some light upon the iodine-tellurium anomaly in the periodic system. In the apparatus employed by him the platinum electrodes (4 square millimeters in area) were placed in separate limbs; the cathode at the bottom of one tube, and the anode somewhat more than half way up the other. Before filling the apparatus with the potassium iodide solution, the cathode was surrounded with solid iodine. During the passage of the current considerable hydrogen was evolved at the cathode, but

[24] Herroun, Phil. Mag. [5] **60**, 91 (1895).
Danneel, Zeit. Electrochem., **4**, 154 (1897).
Kreider, Am. J. Sci. [4] **20**, 1 (1905).
Gino Gallo, Gazz. Chim. Ital., **36**, 11, 116 (1906).

the hydroxyl ion formed was neutralized by the iodine. In order to prevent diffusion of the iodine from cathode to anode, the two limbs were connected by two small tubes (4 mm. diameter) both of which dipped into a wide-mouthed bottle. At the completion of a run a stop-cock at the bottom of the anode limb was opened and the anode solution received in a flask for titration with sodium thiosulphate. A current density of 0.1 ampere per sq. cm. was employed, the amount of iodine produced being only 0.3 gram in each run.

Assuming that the theoretical quantity of each element was freed from the ionic state by the passage of the current, Gallo found the atomic weight of iodine to be 126.89 (Ag = 107.93) as the result of 24 determinations. The maximum deviation was 0.075 percent, the average deviation 0.021 percent. Calculated on the basis of the present value for silver (107.88), iodine becomes 126.83, a difference of 0.07 percent from the accepted value, 126.92.

On the other hand, we may assume that the current frees the theoretical amount of iodine in the iodine coulometer, and consider that the silver coulometer measures the amount of electricity which has passed. Gallo used porous-cup coulometers, and following Richards and Heimrod, made a 0.018 percent correction for included material. The effect of this correction was to lessen the discrepancy between the silver and iodine coulometers, and hence if we compare his results with those of Smith, Mather and Lowry, who made no correction for included material, a difference of 0.09 percent appears. On this basis the iodine coulometer gives the value 96,560 coulombs for the Faraday. The uncertainty in this figure, due to the difficulty in reproducing the exacting conditions in connection with the silver coulometer alone, is at least 0.02 percent.

5. *The Knall-Gas Coulometer.*

Lehfeldt[25] measured the combined volumes of hydrogen and oxygen evolved when a known current was passed through an aqueous solution of an electrolyte and from these data calculated the value of the Faraday. The current was determined by means

[25] Phil. Mag. [6] **15**, 614 (1908).

of the Weston Standard Cell and standard resistances; the author estimated that the quantity of electricity which passed through the coulometer was known to 0.01 percent.[26] In the coulometer, solutions of some twelve different electrolytes were tried. It was found that with a given current, solutions of sodium sulphate and of potassium bichromate gave practically the same volume of gas, while solutions of the other electrolytes gave a smaller quantity. The mean of 16 determinations with solutions of the two electrolytes mentioned above was 0.17394 cc. of gas evolved per coulomb. The average deviation was 0.027 percent, the maximum was 0.058 percent. The value of the Faraday calculated on the assumption that the theoretical quantity of gas is evolved from these solutions is 96,590 coulombs. This value should be considered as an upper limit, however, because no attempt was made to prove the assumption that the theoretical volume of gas was liberated from the sodium sulphate and potassium bichromate solutions.

6. *Summary.*

To facilitate comparison, the results obtained with all of the above coulometers are brought together in Table I. It is evident from this table that the results obtained with the copper, the iodine, and the knall-gas coulometers, in so far as they can be relied upon, all agree in supporting the conclusion that the silver coulometer gives too low a value for the Faraday.

TABLE I.

Coulometer	Observer	Date	Faraday	Precision in Percent (See Note 13)
Silver . . .	Smith, Mather and Lowry . .	1908	96,473	0.0003
Silver . . .	Jaeger and von Steinwehr . .	1908	96,481	0.002
Silver . . .	Laporte and de la Gorce . . .	1910	96,471	<0.001
Silver . .	Rosa, Vinal and McDaniel . .	1911	96,500	<0.001
Copper . .	Richards, Collins and Heimrod	1902	96,535	0.006
Iodine . . .	Gallo	1906	96,560	0.006
Knall-gas .	Lehfeldt	1908	96,590	0.006

[26] *Loc. cit.*, page 621.

PART II.

The Iodine Coulometer.

1. *Purpose and Outline of the Investigation.*

This investigation was undertaken for the purpose of perfecting an iodine coulometer which should equal the silver coulometer in reproducibility and which should be entirely free from all sources of error amounting to more than 0.001 percent, since it is important to determine the value of the Faraday with approximately this degree of accuracy.

An aqueous solution of potassium iodide to which iodine has been added contains both iodide and tri-iodide ions. When a current of electricity is passed through such a solution the reaction,

$$I_3^- + 2\,(-) = 3\,I^-, \qquad (1)$$

takes place in the direction from left to right at the cathode and in the reverse direction at the anode. Hence a cell in which the electrodes are surrounded by such a solution should contain the same total amount of "free iodine" before and after the passage of an electric current. By separating the electrodes and the solutions surrounding them by a conducting solution of an iodide, the changes in the amounts of "free iodine" at the two electrodes can be separately determined, and if the reaction is a perfectly clean cut one, free from all disturbing side reactions, the results at the two electrodes should check each other. The iodine coulometer, therefore, contains within itself the proof of its own correctness, for if it can be shown that identical amounts of iodine are involved in the reactions at both electrodes under varying conditions of concentration and current density, it will establish beyond question the fact that *the only reaction*, involving electricity, which occurs at the anode is that expressed by the equation[27]

$$3\,I^- = I_3^- + 2\,(-). \qquad (2)$$

[27] Or some reaction or set of reactions which are ultimately equivalent to this in the final analysis; which is, of course, just as satisfactory, for the value of the Faraday does not depend upon the mechanism of the reaction, but only upon the final result.

In this particular the iodine coulometer possesses an enormous advantage over the silver coulometer, for, as is well known, no such quantitative proof of the nature of the reaction is possible with the latter coulometer.

It is clear, therefore, that the problem of perfecting an iodine coulometer which will fulfill the above requirements consists chiefly in the satisfactory solution of the following questions:

(1) The discovery of an analytical method for determining "free iodine" in an aqueous solution of an iodide with an accuracy of 0.001 percent.

(2) The perfecting of the mechanical features and arrangement of the apparatus; the nature, form, size, and position of the electrodes, etc.

(3) The measurement of the reproducibility of the anode reaction, for it is this reaction alone which would be ultimately employed in the coulometer, since it involves less manipulation and consequently possesses greater freedom from accidental errors from mechanical sources than does the cathode reaction.

(4) The proof of the reversibility of the reaction as indicated above, by comparing the amount of free iodine formed at the anode with that which disappears at the cathode.

2. *Determination of the Iodine.*

The Analytical Method.—The iodine formed or used up during the electrolysis was determined by titration with a standard solution of arsenious acid. The reaction involved in this titration is the following:

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^- \qquad (3)$$

By making the hydrogen-ion concentration sufficiently small, this reaction can be driven towards the right as completely as desired. If it is made too small, however, an error will be produced, owing to the occurrence of the two following reactions:

$$OH^- + I^-_3 = HIO + 2I^- \qquad (4)$$

and

$$6OH^- + 3I^-_3 = IO^-_3 + 8I^- + 3H_2O. \qquad (5)$$

The success of the method depends therefore upon the control of the hydrogen-ion concentration in the solution at the end of the titration. The method of effecting this control has been described in a previous paper,[28] where the theory and practice of this analytical method, when an accuracy of 0.001 percent is required, have been discussed in detail. The details need not be repeated here.

In all of the titrations performed in connection with this investigation the solution at the end of the titration contained a mixture of Na_2HPO_4 and NaH_2PO_4 in such proportions as to insure a hydrogen-ion concentration of 10^{-7} moles per liter.[29] The method is easily capable of an accuracy of 0.001 to 0.002 percent, and since a definite equilibrium is reached, the end-point is permanent for an indefinite time.[30]

3. *Purification of Materials.*

Water.—The water from which the various chemicals were recrystallized and which was used in making up all of the solutions was conductivity water, obtained by distillation from alkaline permanganate.

Iodine.—The iodine employed was Kahlbaum's "Resublimed," which was freed from possible traces of chlorine, bromine, etc., either by subliming from a concentrated solution of potassium iodide, or by precipitation from such a solution by means of potassium permanganate and sulphuric acid. The iodine was thoroughly dried in a desiccator over sulphuric acid and sublimed in a current of dry air.

Potassium Iodide.—The potassium iodide used was, except where specified, obtained by recrystallizing J. T. Baker's "Special" until it was no longer alkaline to phenolphthalein. The product was pure, and when dried remained so indefinitely. When pro-

[28] Washburn, J. Am. Chem. Sec., 30, 31 (1908).

[29] The calculations carried out in the paper referred to indicated that this value is the most favorable for the titration. As the concentrations of the various substances involved were somewhat different in the present investigation from those employed in the previous calculations, it was thought best to repeat the calculation for the new conditions. This was the more desirable since some of the equilibrium constants involved have been redetermined since the publication of the previous paper. These new values for the equilibrium constants are 5×10^{-2} for reaction (3) above (recently determined in this laboratory by Mr. E. K. Strachan), and 3×10^{-13} for reaction (4) [Bray and Connolly, J. Am. Chem. Soc., 33, 1486 (1911)]. The result of the new calculation was practically identical with that of the previous one, so that no changes in the conditions previously described were necessary.

[30] J. Am. Chem. Soc., 30, 43 (1908).

tected from strong light a saturated solution of the iodide remained colorless for at least twenty-four hours.

Arsenious Acid.—The arsenious acid was obtained by recrystallizing Merck's product from conductivity water.

Sodium Hydroxide.—The sodium hydroxide employed in preparing the standard arsenious acid solution was Kahlbaum's "mit Alkohol gereinigt in Stücken."

Starch Solution.—The starch solution used as an indicator in titrating the iodine was prepared by grinding 6-7 grams of corn starch with a little cold water and adding to a liter of boiling water. After settling in a tall cylinder over night the upper half of the solution was drawn off into test tubes stoppered with cotton wool and was sterilized in an autoclave. Starch solutions thus prepared keep well for six weeks or two months and give an end point of the proper shade.[31]

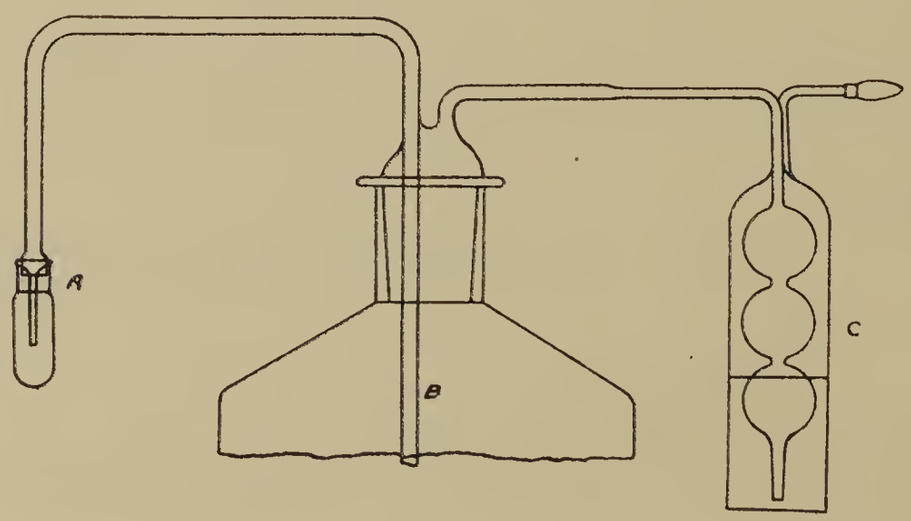


FIG. 1.

4. *Preparation of the Standard Solutions.*

The Sodium Phosphate Solution.—This solution was prepared by dissolving J. T. Baker's C. P. di-sodium phosphate ($Na_2HPO_4.12H_2O$) in about five times its weight of water. The solution was kept in a ten liter stock bottle from which the required amount was syphoned off and poured into the flask in which the titration was performed.

The Standard Iodine Solution.—The standard iodine solution used at the cathode in the coulometer was prepared by dissolving

[31] See Washburn, J. Am. Chem. Soc., 30, 42 (1908).

about 680 g. of iodine and 480 g. of potassium iodide in 700 grams of water. This solution was kept protected from the light in a stock bottle, into the neck of which was ground a delivery tube which reached to the bottom of the bottle. Air previously bubbled through a wash bottle containing some of the same solution was used to force the solution out of the stock bottle. To prevent loss of iodine or water vapor the end of the delivery tube and that of the tube through which pressure was applied were protected by means of glass caps. The arrangement is shown in Fig. 1. The solution was made up at least eight months before it was used for the experiments recorded below.

The Dilute Iodine Solution.—This solution, which was used only when the end point was overstepped with the arsenious acid, was 0.005 normal. It was prepared by weight from the above solution and was kept in a bottle into whose neck was ground a glass stopper which carried a Göckel automatic burette.

The Standard Arsenious Acid Solution.—The standard arsenious acid solution was prepared by dissolving 530 grams of arsenic trioxide in a solution containing about 650 grams of sodium hydrate. When all the trioxide had dissolved, the solution was filtered through asbestos and diluted until it was approximately 0.9 normal.

5. Standardization and Behavior of the Standard Solutions.

Treatment of the Standard Iodine Solution.—Since this solution was employed at the cathode in the coulometer, it was deemed best to duplicate, in standardizing it, the same conditions to which it was subjected during use in the coulometer. Hence the proper amount of the solution was weighed out, transferred to the coulometer and allowed to stand over night in contact with the electrode. The following day it was withdrawn and received in a flask containing a weighed amount of the standard arsenious acid solution and the titration completed as described below. The method of procedure employed in handling the iodine solution duplicated exactly that employed during the regular runs with the coulometer and is fully described in the next section.

Weighing out the Arsenious Acid Solution.—The standard arsenious acid solution was kept in a 15-liter bottle which stood beside the balance case in a constant temperature room in the basement of the building. The stock-bottle was provided with a rubber stopper carrying a delivery tube which could be swung directly over the mouth of a flask upon the pan of the balance. This arrangement permitted any desired amount of the solution to be weighed out into the flask very exactly. The air or gas which entered the stock bottle was bubbled through a wash bottle containing some of the same solution. Liter Erlenmeyer flasks, of white glass, were employed for weighing out the arsenious acid solution, a similar flask being used as a counterpoise. The quantity of solution weighed out each time was always from 0.05 to 0.1 gram less than the exact amount required to react with the iodine solution in the titration.

Completion of the Titration.—After the flask containing the arsenious acid solution had assumed constant weight the necessary amount of the di-sodium phosphate solution was added, the flask was connected to the coulometer and the iodine solution drawn over into it, as described in the next section. The solution was then thoroughly mixed and the titration completed with a dilute solution of arsenious acid. This solution was prepared by diluting about 5 grams of the concentrated solution to exactly 100 times its weight. The burette from which the dilute solution was delivered was calibrated by the use of this dilute solution. On account of the possibility of an error due to the oxidation of the dilute solution a fresh lot was prepared every two or three weeks; the maximum change in strength due to oxidation was estimated to be 0.5 percent. Practically never was it found necessary to use more than 10 cc. of this solution to complete a titration, and since 1 cc. corresponded to about 0.02 percent of the total arsenious acid used in the titration, the error due to the change in strength of the dilute solution was never greater than 0.001 percent.

Under the conditions employed it was found that equilibrium between the iodine and the arsenious acid was attained almost immediately. The reaction between the starch and the tri-iodide ion is, however, much slower. Hence in the titrations the dilute

arsenious acid solution was added until the solution was colorless; in a good light and with a flask of water as a standard, the disappearance of the yellow iodine could be judged to about 0.10 cc. of the dilute arsenious acid solution, *i. e.*, to about 0.002 per cent. As a check, however, 5 cc. of the starch solution was then introduced, and the dilute iodine solution (0.005 normal) added, until on standing for a few moments the proper pink-colored end-point remained. This end-point is a little more sensitive than the other. About 0.4 cc. of the 0.005 normal iodine solution was required to change from one end-point to the other.

Temperature has but a slight effect upon the end-point. After finishing one of the titrations, the solution was warmed to 35° C. and the pink-colored end-point reached. On cooling to 15° C, only 0.15 cc. of the 0.01 normal arsenious acid solution was required to give the same colored end-point. This represents a change of 0.003 percent for the 20°, and hence no attempt was made to regulate the temperature of the solutions during titration.

Oxidation of the Arsenious Acid Solution.—When the stock solution of arsenious acid was first made up it was fitted with a Göckel burette for delivering approximately the desired quantity of the solution into the flasks to be weighed. With this arrangement irregular results regarding the strength of the solution were obtained. It was noticed, however, that in general the solution tended to become weaker with time, indicating oxidation.[32] When this was noticed, the solution was protected from the light and kept under hydrogen. The hydrogen was generated from C. P. zinc and sulphuric acid. It was washed by bubbling through solutions of lead nitrate and alkaline permanganate and then through a wash bottle containing some of the arsenious acid solution. To free the solution from air the pressure upon it was three times reduced as far as possible with a water pump and then increased to that of the atmosphere by slowly bubbling hydrogen through the liquid. The stock bottle remained attached

[32] The irregularity of the results may be explained by the fact that the burette was in general filled to the top before each titration, but was usually only a little more than half emptied. The other half of the solution, which had become pretty well saturated with air, then lay for an indefinite period in the lower part of the burette until the next portion was drawn off. This portion of the standard solution then oxidized more rapidly than that in the stock bottle, and thus irregular results were obtained. The rate of oxidation of the stock solution was estimated to be about 0.02 percent per day.

to the hydrogen generator, so that as the solution was withdrawn it could be replaced by hydrogen.

This procedure did not, of course, remove the last traces of dissolved oxygen from the solution, nor is hydrogen prepared in the above manner entirely free from oxygen. It was expected, however, that the partial pressure of the oxygen would be sufficiently reduced to materially decrease the rate of oxidation. This was found to be the case, the rate of oxidation being reduced from 0.02 to less than 0.003 percent per day. This rate was,

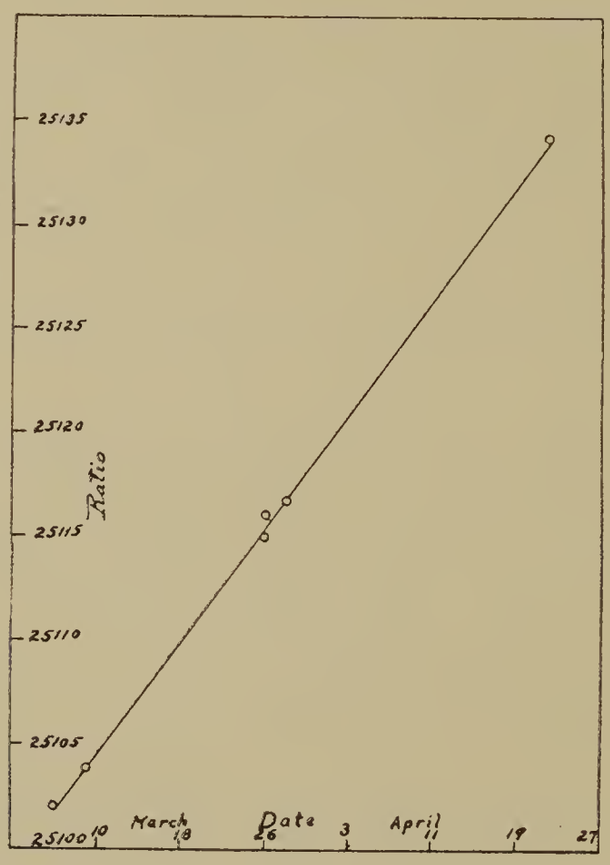


FIG. 2.

moreover, perfectly constant, as is evident from the data in Table II, which represent the results of comparisons of the arsenious acid solution with the standard iodine solution extending over a period of 47 days. In the first column is given the number of the comparison, in the second the date on which the arsenious acid solution was drawn from the stock bottle for immediate titration. The third and fourth columns give the weights of the iodine and arsenious acid solutions, respectively, which were used. The number of grams of arsenious acid solution required

to titrate one gram of the iodine solution is given in the fifth column. In the sixth column is given this value as calculated for the day in question (see below). The seventh column contains the percentage difference between these values as found and as calculated.

These results are shown graphically in Fig. 2, in which the times (day of month) are plotted as abscissae and the ratio of the two solutions as ordinates. The slope of the curve corresponds to a rate of oxidation of 0.00273 percent per day. The calculated value of the ratio of the two solutions at any given time (see column six, Table II) was read off from the curve; it was estimated to be known to 0.001 percent.

TABLE II.

Ratio of the Arsenious Acid and Iodine Solutions.

No.	Date	Grams of Iodine Solution	Grams of Arsenious Acid Solution	Ratio		Difference Percent
				Found	Calculated	
1	March 6	20.3883	51.1787	2.51020	2.51017	0.0012
2	" 9	23.0459	57.8530	2.51038	2.51038	0.0000
3	" 11	19.1883	48.1824	2.51105	2.51051	(0.02)
4	" 19	21.9252	55.0486	2.51080	2.51105	(0.01)
5	" 26	26.0033	65.3085	2.51160	2.51154	0.0024
6	" 26	23.0414	57.8686	2.51150	2.51154	0.0016
7	" 28	27.0322	67.8960	2.51167	2.51167	0.0000
8	April 22	24.6357	61.9202	2.51342	2.51339	0.0012
				Average deviation . . .		0.00106

In calculating the average deviation from the mean for column six of the table, the results of standardizations 3 and 4 were rejected; the former because it was subsequently found that the potassium iodide used in making up the solutions for the coulometer already contained some iodine. The result of standardization 4 was rejected, because the deviation from the mean was more than four times as large as the average of the deviations of the other results. All of the results of the investigation of the behavior of the iodine coulometer which are recorded in Table II and this table, and the corresponding graph, were

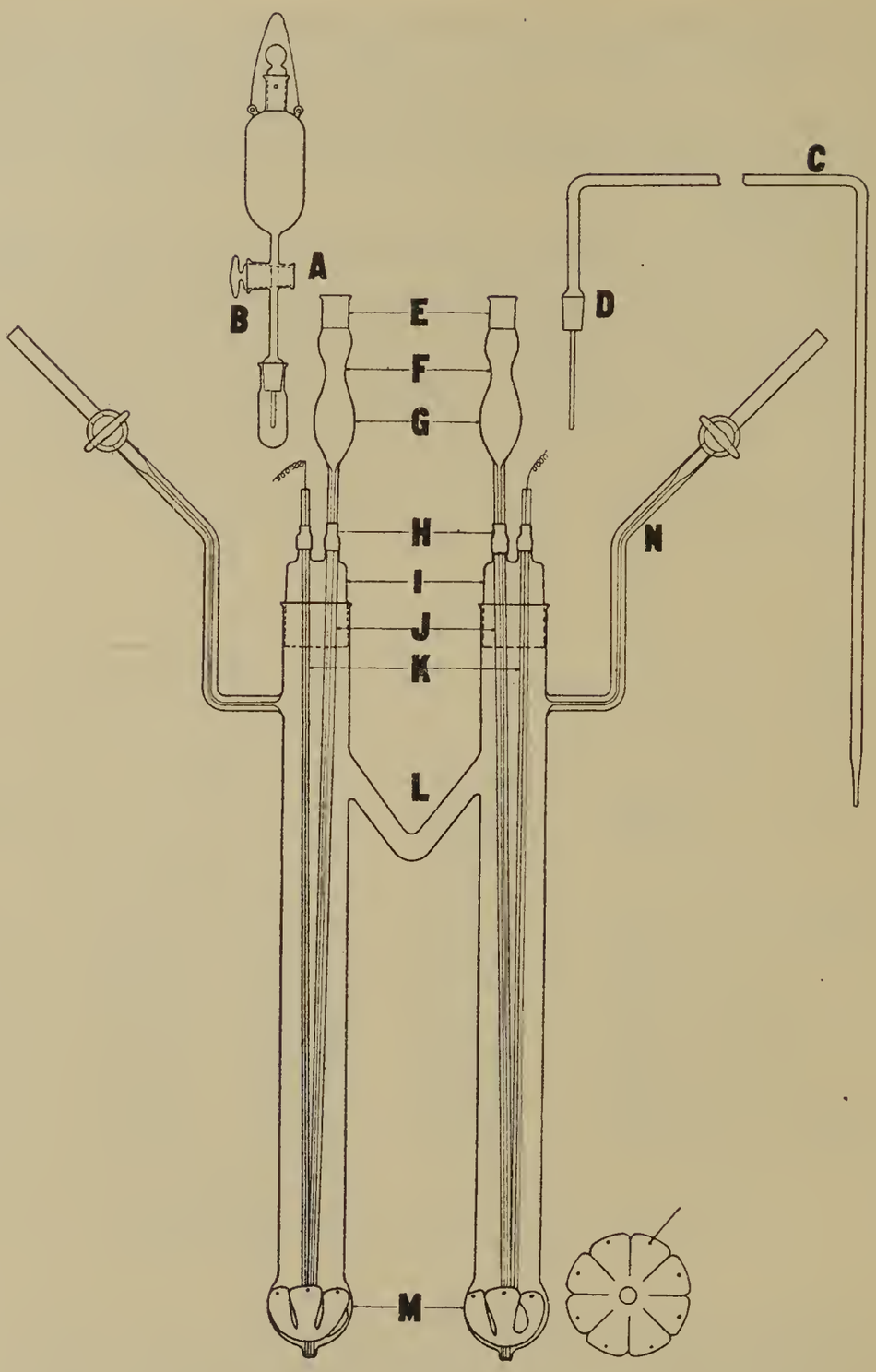


FIG. 3.

employed in computing the strength of the arsenious acid solution for any desired date.

From the value of the equilibrium constant[33] for the reaction between oxygen and arsenious acid in solution it was found on

[33] The value of this constant was computed from the E. M. F. of the normal iodine electrode, the E. M. F. of the oxygen cell, and the E. M. F. of the normal arsenious-arsenic electrode, the latter quantity having been determined in this laboratory recently by Mr. E. K. Strachan.

calculation that in order to prevent entirely the further oxidation of the stock solution it would be necessary to reduce the partial pressure of oxygen to 10^{-60} atmospheres. While it is quite possible to obtain hydrogen of this degree of purity or sufficiently free from oxygen to prevent any appreciable oxidation of the arsenious acid, it was not deemed necessary to do at this stage of the investigation, as no error of any importance was introduced in correcting for the oxidation as explained above.

6. *The Iodine Coulometer and the Method of Procedure.*

The Coulometer.—The iodine coulometer as finally perfected is shown in Fig. 3. It consists essentially of two upright limbs connected by a V-tube. At the bottom of each limb is placed an electrode. The caps *I* are ground into the upper parts of the limbs. Two short tubes are sealed into the top of each cap; through one runs a glass tube *K* which carries the electrode connection, and through the other a capillary tube *J* which passes through a hole in the center of the electrode to the lowest point of the limb. A short sleeve of rubber tubing *H* is fitted over these tubes, thus making an air-tight joint with the cap, and yet permitting the capillary tube, or this and the cap together, to be withdrawn without disturbing the electrode. The side tube *N*, with which a leveling bulb may be connected, serves for filling the apparatus and for adjusting the level of the solution in the capillary tubes.

The coulometer was supported in a battery jar which was filled with water to the level of the V-tube. No attempt was made to keep the temperature of the bath constant, but the arrangement eliminated convection currents and stirring due to sudden temperature changes. A white plate placed behind the coulometer served to detect any diffusion of the iodine solutions.

The Electrodes.—The electrodes were of platinum-iridium foil. They were cut (see Fig. 3) so that they would fold up while being introduced into the limb of the coulometer and then in position spread out so as to fill the bulb *M* at the bottom of the limb. To assist in removing the electrode when necessary, a small hole was made in each of the leaflets into which a wire could be hooked. A hole of 0.7 cm. diameter was cut in the

center of the electrode, and through this the tip of the capillary tube passed. The effective area of each electrode was about 50 sq. cm.

The electrical connections were made by means of a wire welded on to one of the leaflets of the electrode and sealed into a glass tube which passed out through the cap at the top. In the case of one of the electrodes the connecting wire was woven through slits in one of the leaflets instead of being welded onto it. This gave greater flexibility and ease of manipulation in introducing the electrode as well as eliminating the danger of breaking the connection. A little paraffin was melted and run down from the tube carrying the electrical connections; this served to hold in place the mercury which formed part of the circuit.

Filling the Coulometer.—After the electrodes are in place, the whole coulometer is filled by means of the side tube *N* to a little about the level of the V-tube *L* with a ten percent solution of potassium iodide. Care is taken that no air is entrapped around the electrodes and that no bubbles adhere to their surfaces. The leveling bulb which is attached to the side *N* is then raised until the solution rises to the top of the capillary tube *J*, which opens rather abruptly into the bulb *G*.

(a) The Anode Limb.—At the anode side about 25 cc. of a concentrated solution of potassium iodide (one gram of salt to one gram of water), previously freed from air by boiling, is next run into the bulb *G* and allowed to cover the electrodes to a depth of about 5 cm. During the electrolysis the opening *E* is protected by means of an inverted test tube.

(b) The Cathode Limb.—In a similar manner 6 to 8 cc. of the same concentrated potassium iodide solution is then introduced below the solution in the cathode limb. This solution is immediately followed by about 45 grams (20 cc.) of the standard solution of iodine in potassium iodide. This is run in from the weight burette (see below) and care is taken that no air is drawn down the capillary. The ground glass joint *B* between the burette and its cap just fits into the bulb on the capillary at *F*, the tip of the burette extending well below this point. As soon as the burette is empty it is withdrawn and the tip protected by means

of the glass cap. Loss of iodine from the bulb *G* is prevented by immediately placing the delivery tube *C* in position. The ground joint between *D* and *E* is lubricated with a little phosphoric acid.[34]

The leveling bulb attached to the side tube *N* serves to regulate the flow of solution down the capillary tube, and makes it possible to surround the electrodes with a dense solution without causing any appreciable mixing with the dilute solution above.

(c) The Weight Burette.—The weight burette employed in introducing the standard solution into the cathode limb is shown in Fig. 3. It is filled by suspending it in such a way that the delivery tube (see *A*, Fig. 1) of the stock bottle containing the iodine solution is well within the neck of the burette.

The solution is then forced over by air pressure. After filling, the burette is transferred to the balance case and carefully weighed, using a similar burette as a counterpoise.

The stop-cock *A* of the burette is lubricated with a drop or two of vaseline. This vaseline had been shaken up with a strong solution of potassium iodide, allowed to stand during the summer, washed with a dilute sodium thiosulphate solution until it was free from iodine, and finally distilled under reduced pressure.

Removal and Analysis of the Electrode Portions.—The current is passed through two iodine coulometers, a silver coulometer, and a milliammeter, in series. The silver coulometer was not handled with any particular care, as it was employed merely for the purpose of calculating the approximate amounts of the arsenious acid solution required for titrating the electrode portions. The time required for a run varied from about 15 hours to 65 hours. During this time little mixing of the iodine solution at either electrode with the dilute solution above it occurred. At the anode side no iodine could be detected higher than one-fourth of the distance up the limb. At the cathode side the iodine was rarely visible one-half of the way and usually not more than one-third of the way up the limb. The few cubic centimeters of the concentrated potassium iodide solution which were introduced through the capillary at the cathode side were

[34] In rinsing out the bulb after a run this phosphoric acid is washed into the bulb *G* and then sucked over into the flask, in which the titration is performed. The presence of this acid does not effect the titration; in fact, it was found that the addition of 5 cc. of the acid employed did not affect the result by 0.001 percent.

found to diminish materially the migration in this limb. This is due to the fact that the layer of strong potassium iodide solution greatly diminishes the potential gradient, and hence also the migration velocity of the tri-iodide ions.

When about 0.05 Faraday of electricity has passed, the circuit is broken. The approximate amount of electricity which has passed through the system is calculated from the weight of silver deposited in the silver coulometer, and thus are found the approximate amounts of standard arsenious acid solution necessary to titrate the cathode and anode portions respectively. About 0.05 gram less than the required amount of the arsenious solution is then weighed out into a liter Erlenmeyer flask as described above, and the flask is fitted to the delivery tube *C* in such a way that the tip of the delivery tube is well below the level of the liquid in the flask. On applying a gentle suction to the flask the electrode portion is sucked over through the capillary tube and the delivery tube. The dilute solution of potassium iodide in the upper part of the limb completely washes the iodine from around the electrode and the latter half of the solution sucked over into the flask shows no color. The solution in the flask is thoroughly mixed and the titration completed in the manner already described.

7. Precision of the Anode Reaction.

Table III shows the agreement obtained between two iodine coulometers in series. All of the data obtained with reference to this point are included in the table. On account of an accident, one of the anode portions in runs 6, 10 and 11, was not titrated. In the calculation of the average deviation from the mean, the results of runs 5, 7 and 8 were not employed. The first was rejected because the deviation was more than four times as great as the average of the others; the results of runs 7 and 8 were not used for the reason explained below. The average deviation from the mean as calculated from the results given in this table is just equal to the uncertainty in judging the end-point.

Permissible Current Density.—The object of runs 7 and 8 was to make certain that the current densities employed were not too large. In one coulometer an anode of the usual size (50 sq. cm. total area) was employed, while the total surface of

the second was but 8 sq. cm. In these two experiments the larger electrode gave the greater amount of iodine. The difference is, however, but slightly greater than the average of the other experiments, and the result obtained from but two runs cannot be regarded as conclusive. It will be seen, however, that a current density of 0.005 ampere per sq. cm. is allowable; in all the runs except these two, the current density was between 0.0004 and 0.0015 ampere per sq. cm. and hence well below this possibly-limiting value.

TABLE III.

Reproducibility of the Anode Reaction.

No.	Date	Current (Milliamperes)	Grams of Arsenious Acid Solution			Deviation from the Mean (Percent)
			Anode No. 1	Anode No. 2	Mean	
1	March 4	37	58.6584	58.6598	58.6591	0.0012
2	" 6	40	52.6863	52.6841	52.6852	0.0021
3	" 9	20	*57.2657	57.2622	57.2640	0.0030
4	" 11	40	55.1379	55.1404	55.1391	0.0023
5	" 16	40	60.7797	60.7682	60.7740	(0.0095)
7	" 21	43	65.5012	65.4968	65.4990	(0.0034)
8	" 23	68	63.3568	63.3517	63.3542	(0 0041)
9	April 7	45	65.2055	65.2100	65.2077	0.0035
12	" 20	70	62.2437	62.2415	62.2426	0.0018
13	" 27	80	59.8340	59.8345	59.8342	0.0004
			Average deviation from the Mean .			0.0020

* Baker's "Special" potassium iodide, without further purification, was used in preparing the solutions for anode No. 1.

8. Comparison of the Reactions at Anode and Cathode.

For the purpose of comparing the amount of iodine formed at the anode with the amount which disappears at the cathode, a series of runs was made in which the current was passed through two iodine coulometers connected in series. The anode portion from both coulometers were then titrated, as was also the cathode portion from one of them, that from the other being rejected.[35]

In Table IV are given the results of these comparisons. In the first column is given the number of the run, in the second

[35] This was necessary because only three suitable electrodes were available at the time these comparison runs were made.

column the day on which the arsenious acid solution was withdrawn from the stock bottle for the titration, and in the third column the current in milliamperes. The next column gives the weight of the concentrated standard iodine solution which was introduced from the weight burette into the cathode limb. The fifth column gives the mean weight of arsenious acid solution used to titrate the two anode solutions (see Table III). For experiment No. 5, however, the data for both anode solutions are given separately, since as pointed out above (Table III and discussion) the difference between them is too large to be accidental and one value is probably correct and the other one incorrect. The weight of arsenious acid solution required for the cathode portion is given in column six. The next column gives the total amount of arsenious acid solution used in titrating both the cathode and the anode portions. The eighth column gives the quantity of this solution which should be required for the titration of the amount of the standard iodine solution used, as calculated from its weight and from the ratio of the two standard solutions as read off from the curve (Fig. 2) for the day in question.

The results show that, within the limit of error of the analysis (0.002 percent), the same amount of iodine is formed from iodide ions at the anode as is converted into iodide ions at the cathode.

TABLE IV.

Comparison of Anode and Cathode Reactions.

No.	Date	Current (Milliamperes)	Grams of Iodine Solution	Grams of Arsenious Acid Solution				Deviation (Percent)
				Anode	Cathode	Total Found	Total Calc.	
4	Mar. 6	40	47.0374	52.6852	65.4103	118.0955	118.0719	*(0.020)
2	" 11	40	45.6123	55.1391	59.3737	114.5128	114.5100	0.0024
5a	" 16	40	45.4523	60.7795	53.3585	114.1382	114.1238	*(0.013)
5b	" 16	40	45.4523	60.7682	53.3585	114.1267	114.1238	0.0025
6	" 19	20	44.6216	48.3080	63 7373	112.0453	112.0471	−0.0016
7	" 21	43	45.6662	65.4990	49.1721	114.6711	114 6763	−0.0045
				Average deviation				0.0028

* Rejected in computing the average deviation.

The iodine coulometer is, therefore, certainly free from any constant source of error amounting to more than 0.002 percent. The reproducibility of the reaction at the anode is all that could be desired and fulfils all of the requirements necessary for a trustworthy determination of the value of the Faraday within 0.001 percent.

9. *Summary and Conclusions.*

The results of the foregoing study of the iodine coulometer as a precision instrument may be summed up by comparing its advantages and disadvantages with those of the silver coulometer.

1. *Reproducibility.*—Practically the same for both coulometers, 0.001 to 0.002 percent.

2. *Purity of Materials.*—(a) For the silver coulometer the silver nitrate requires special purification and must be very carefully protected from dust or organic matter of any kind.

(b) A filtered solution of commercial C. P. potassium iodide is satisfactory for the iodine coulometer. It needs only to be protected from a strong light.

3. *Electrochemical Equivalent.*—The number of grams per coulomb is about the same for both coulometers, with the advantage in favor of the iodine coulometer.

4. *Influence of Electrode products.*—(a) The anode products constitute an annoying source of error in the case of the silver coulometer, the employment of porous-cups being necessary in order to diminish it. These cups require very careful treatment and are possibly not entirely effective, especially if the electrolysis is a prolonged one. (b) The iodine coulometer is not subject to this source of error.

5. *Included Material.*—(a) The silver deposit contains included material which must be separately estimated and corrected for by a rather tedious process.[36] An appreciable degree of uncertainty is also involved in making this correction, due to the fact that the included material contains both water and silver nitrate. (b) This source of error and uncertainty does not affect

[36] *Cf.* Duschak and Hulett, *loc. cit.*

the iodine coulometer, since no deposit is obtained in that instrument. A quantity of very pure and dry iodine must, however, be prepared for standardization purposes. This is fully as tedious a process as the determination of the correction for inclusion in the case of the silver coulometer, but it involves no element of uncertainty and does not need to be performed in connection with every electrolysis. In fact, 25 grams of pure iodine can be easily made to suffice for the measurement of a quantity of electricity which would give four or five hundred deposits of silver of 5 grams each, if measured with a single silver coulometer.

6. *Reversibility.*—(a) The reaction in the silver coulometer is not reversible. The reaction at the anode is complicated by the formation of complex ions which not only make it impossible to employ this electrode as a check on the cathode, but also constitute a source of error at the latter electrode, as explained above. There is no means of knowing for certain under what condition (if any) the process at the cathode deposits pure silver solely by the reaction, $Ag^- + (-) = Ag$. (b) The reaction in the iodine coulometer is perfectly reversible, the same result being obtained from both electrodes, which may be regarded as conclusive proof of the purity of the reaction, $3I^- = I^-_3 + 2(-)$, occurring at the anode. Certainty upon this point is of the utmost importance in determining the value of the Faraday.

PART III.

Comparison of the Iodine and Silver Coulometers, and Determination of the Value of the Faraday.

1. *Introduction.*

Owing to lack of time no attempt was made in connection with the present work to undertake the final determination of the value of the Faraday by means of the iodine coulometer, as this would have involved the preparation of new and more stable standard solutions and the preparation of perfectly pure, dry iodine, as well as considerable preparatory work in connection

with the silver coulometers. It is our intention to proceed with this more extensive investigation during the coming year.

A provisional comparison of the iodine and silver coulometers employing material already at hand was, however, undertaken, and although an accuracy of more than 0.01 or 0.02 percent was not aimed at, the results obtained seem worth recording, as they have an important bearing upon the silver coulometer.

2. *Purity of Materials.*

Iodine.—The iodine employed in standardizing the arsenious acid solution was prepared as already described. (Part II). For the present purpose it was necessary to dry it thoroughly. A portion of that employed for the standardization had been standing over sulphuric acid for eight months. A second sample was similarly dried for one month. The weighing bottle was filled by subliming the iodine into it in a current of dry air, in an apparatus especially constructed for this purpose by Dr. Grinnel Jones of this laboratory. In some instances this sublimation was repeated. The air was dried by passing it through a number of towers filled with glass beads moistened with sulphuric acid. It is improbable that the iodine thus obtained could have contained 0.01 percent of moisture.

Silver Nitrate.—The silver nitrate for use in the silver coulometers was prepared by several recrystallizations of Kahlbaum's product, from conductivity water containing an excess of pure nitric acid.

The crystals were drained by suction each time on a Buchner funnel without employing any filter paper. In order to remove the excess of nitric acid the crystals were fused in a porcelain casserole. As soon as the last trace of nitric acid had been driven out (which was readily noted by an immediate quieting and clearing of the surface), the fused silver nitrate was poured into a platinum crucible floating in water. The product thus obtained was perfectly white and gave a perfectly neutral solution.

Standardization of the Arsenious Acid Solution.—Two slightly different methods were employed in standardizing the arsenious acid solution against iodine. In the first of these methods, the

weighing bottle containing the dry iodine (about 5 grams) was introduced into a flask containing approximately the required amount of the standard arsenious acid solution and was opened below the surface of the solution. In order to duplicate the conditions employed in analyzing the electrode portions, and also to hasten the solution of the iodine, about 20 grams of potassium iodide was then added. When the iodine had completely dissolved, the required amount of di-sodium phosphate solution was poured into the flask and the titration completed with the dilute arsenious acid solution.

TABLE V.

Standardization of Arsenious Acid Solution.

Date	Grams of Iodine	Grams of Arsenious Acid Solution	Grams Arsenious Acid Solution per Gram Iodine		Deviation from Mean (Percent)
			Found	Calculated to April 14	
April 9	4.73094	42.6330	9.0115	9.0128	0.012
" 9	6.08782	54.8667	9.0125	9.0138	0.001
" 10	5.03221	45.3625	9.0144	9.0154	0.017
" 10	4.19609	37.8086	9.0104	9.0114	0.028
" 16	8.17313	73.6790	9.0148	9.0143	0.004
" 24	5.28330	47.6270	9.0146	9.0121	0.020
" 26	5.88452	62.0797	9.0173	9.0143	0.004
" 26	4.66718	42.0788	9.0159	9.0130	0.010
" 28	7.05761	63.0516	9.0190	9.0153	0.015
" 29	6.13542	55.3434	9.0203	9.0166	0.030
			Mean	9.0139	
			Average deviation from Mean		0.014
			Precision $= \frac{0.014}{\sqrt{10}} =$		0.0044

In the second method, seven or eight grams of potassium iodide was placed in the weighing bottle and not quite enough water to dissolve this salt was then added. The stoppered bottle was left in the balance-case for two or three hours and then weighed. Five or six grams of iodine was then quickly added and the bottle again weighed.[37] It was next introduced into the flask containing the arsenious acid and opened under the solution.

Both methods gave practically the same results. The results of all the standardizations made are shown in Table V. Those

[37] The weight of water lost by evaporation from this concentrated solution during the introduction of the iodine was very small; blank experiments showed that it was not over 0.3 mg., and a correction for this was applied.

of April 24th and 26th were made by the second method and the others by the first. The figures in the fifth column were calculated to April 14th by correcting for the rate of oxidation (0.00273 percent per day) of the arsenious acid solution as explained in Part II. A standardization of the arsenious acid solution was made in connection with each of the comparison runs with the iodine and silver coulometers.

3. The Silver Coulometers.

The quantity of electricity which passes through the system was determined by means of two silver coulometers. These were practically the same type as those employed by Smith, Mather and Lowry, and the various conditions and methods of procedure employed by them were duplicated as closely as possible.

The anodes were of pure mint silver. They were surrounded by filter paper cups, suspended by means of insulated platinum wire. A 15 percent solution of silver nitrate was employed in the coulometers. At the end of every second run the solution was rejected and a fresh lot employed for the next experiment.

Each of the bowl-shaped platinum vessels, which served as cathodes, weighed about 50 grams and was 10 cm. in diameter at the top. Bowl *A* was 4.5 cm. in depth and held, when full, 275 cc.; bowl *B* was 5.5 cm. in depth and held 350 cc. The volumes of silver nitrate solution which were used in the coulometers during a run were about 150 cc. and 200 cc. respectively. Before using, the bowls were thoroughly washed with nitric acid and water and dried in an electric oven at 160°. A third bowl, which was of practically the same dimensions and weight, and which was used for counterpoise, was similarly treated. On the completion of a run the electrolyte was removed from the bowls by means of a pipette. They were rinsed five or six times with water and finally filled with water and allowed to stand over night. Three or four rinsings with water followed, after which they were heated in an electric oven at 160° for one hour. After cooling in a desiccator for several hours, they were placed on the balance pan and allowed to come to a constant weight. The silver deposit was removed from the bowls by means of

nitric acid. The bowls were then thoroughly washed and heated in the oven in preparation for the next experiment.

Weights and Balances.—The gold-plated brass weights which were used in this investigation were calibrated and standardized by the Bureau of Standards. The arsenious acid solution was weighed into liter flasks on a Ruprecht balance, sensitive to 0.1 milligram with this load. All the other weighings were made on a Becker balance sensitive to 0.05 milligram. The weights of iodine and silver were reduced to *vacuo* by adding 0.0099 percent to the apparent weight of iodine and by subtracting 0.0031 percent from that of silver.[38]

4. Comparison of the Iodine and Silver Coulometers and the Determination of the Faraday.—Results and Conclusions.

In this series of experiments a current of electricity was passed through two iodine coulometers and two silver coulometers connected in series. The results are shown in Table VI. The amount of electricity which passed through the system (column 7) was calculated by dividing the mass of silver (column 6) by 0.00111827, which Smith and Lowry found to be the increase in weight of the cathode bowls per coulomb, under similar conditions. In order to calculate the amount of iodine formed, the amount of arsenious acid solution which was required for the titration was calculated to April 21st by correcting for the rate of oxidation. The result is given in column 9. The number of grams of iodine formed (column 10) was then obtained by dividing these values by 9.0139, the number of grams of arsenious acid solution corresponding to one gram of iodine (see Table V). The electrochemical equivalent as given in the tenth column was found by dividing the number of milligrams of iodine formed by the number of coulombs of electricity which had passed. The corresponding values for the Faraday were obtained by dividing the results in column 10 into the atomic weight of iodine, 126.92.[39]

The following facts with reference to the results shown in Table VI should be noted:

[38] In the original calculation the weight of iodine was reduced to *vacuo* by subtracting 0.0099 percent of its apparent weight. We wish to thank Professor G. P. Baxter, of Harvard University, for calling our attention to this error.

[39] Baxter, J. Am. Chem. Soc., **32**, 1602 (1910).

(1) The mean value for the Faraday, 96,524 coulombs, given in column 13, has a precision of 0.005 percent. The average deviation of the individual results from the mean is 0.010 percent and the maximum is only 0.012 percent. These deviations are caused by the silver coulometer, not by the iodine coulometer.

TABLE VI.

1	2	3	4	5	6	7
No.	Date	Current (Milliamperes)	Silver Deposited in Coulometer			Coulombs
			Bowl A	Bowl B	Mean, Corr. to Vacuo	
9	Apr. 7	45	*6.15330	*6.15285	6.15289	5502.17
10	" 10	50	6.50800	. . . .	6.50779	5819.52
11	" 14	40	5.94555	5.94500	5.94510	5316.35
13	" 27	80	. . . .	5.64250	5.64232	5045.75

1	8	9	10	11	12	13
No.	Grams Arsenious Acid Solution		Iodine	Ratio Ag : I	Electro-chemical Equivalent of Iodine, Milligrams per Coulomb	Faraday I = 126.92
	Used	Calc. to April 14				
9	65.2077	65.2201	7.2355	0.85037	1.31503	96,515
10	68.9599	68.9674	7.6512	0.85055	1.31476	96,535
11	63.0049	63.0049	6.9898	0.85054	1.31478	96,534
13	59.8342	59.8119	6.6355	0.85035	1.31508	96,512
			Mean . .	0.85045	1.31491	96,524
					Av. deviation .	0.010%

* The silver nitrate employed in this run was Kahlbaum's product once recrystallized from conductivity water.

(2) The results with the iodine coulometer confirm the conclusion, already reached, that the silver deposit obtained in the silver coulometer, even under the best conditions, is greater than that required by the reaction, $Ag^+ + (-) = Ag$.

(3) If instead of using the International Atomic Weights for 1912, as above, we employ the ratio of silver to iodine (0.849906)

as directly determined by Baxter,[40] our results then give 1.11755 milligrams per coulomb as the true electrochemical equivalent of silver. This is 0.06 percent lower than the value obtained by Smith, Mather and Lowry and 0.04 percent lower than the recent result of Rosa, Vinal and McDaniel (see Table I).

(4) Although we have no reason to believe that our results are affected by any source of error amounting to more than 0.02 percent, they are, perhaps, too few in number to justify the conclusion that the value, 96,524 coulombs, is correct within this limit. We believe, however, that the evidence presented in the foregoing pages justifies the statement that the value of the Faraday is certainly *greater* than 96,500 coulombs and that the true electrochemical of silver is certainly *less than* 1.1180 milligrams per coulomb.

Laboratory of Physical Chemistry,
Univ. of Illinois, Urbana, Ill.,
June 27, 1912.

DISCUSSION.

DR. W. LASH MILLER: All of us who work in electrochemical laboratories have occasion to repeatedly use coulometers, and it is extremely good news that with such a simple apparatus as we have seen described we may feel that we can rely on the results; that they are not only reproducible, but, as Prof. Washburn puts it, they are right. I never had such a feeling, and I think as we find that out most other coulometers will be rejected in favor of this one.

A MEMBER: I would like to ask whether the electrochemical equivalent of iodine has been determined as accurately as that of silver?

PROF. E. W. WASHBURN: The results I have just given you are the only results for the electrochemical equivalent of iodine that have ever been obtained with anything like the precision which we have been able to secure in this investigation.

[40] J. Am. Chem. Soc., **32**, 1602 (1910).

PROF. G. A. HULETT: I feel that this is exceedingly important work, because almost all the previous work has been done with one electrolyte, a silver nitrate solution. I think the thing that would particularly appeal to everyone who has worked along these lines is the fact that you have a reversible reaction; that is, you can use either anode or cathode. This is not possible in any other form of precision coulometer and is a very important thing.

It seems to me that Dr. Washburn's coulometer should be compared as accurately as possible with the silver coulometer, because we can now not only obtain reproducible results with the silver coulometer, but also can determine the inclusions accurately; and, if one determines the inclusions in the deposit, I do not think it matters very much whether one uses extra pure silver nitrate or not. By using ordinarily pure materials and determining the inclusions you will have results which would give you a basis for an exact comparison between electrochemical equivalent of silver and iodine. It would make an interesting comparison with the chemically determined equivalents. We thought we had such a comparison from the results from our cadmium coulometer, but the chemical equivalents at once came into the question. The chemical equivalent of cadmium is given as 56.20 while we found the electrochemical to be 56.15. There is one disadvantage in the iodine coulometer from the standpoint of its use as a coulometer; as I understand it the internal resistance is very considerable, and you use rather small current.

PROF. WASHBURN: One-tenth of an ampere in this investigation.

PROF. HULETT: One big advantage in the silver coulometer is its low internal resistance, so you can use a great variation of current density, and we have not been able to detect sources of error due to these variations.

PROF. WASHBURN (*Contributed*): Our experiments indicate that considerably higher currents could be employed if desired, especially if a larger electrode be employed. I am sure that the iodine coulometer will fully equal the silver coulometer in this respect.

A paper read before Section Xa: Electrochemistry of the Eighth International Congress of Applied Chemistry, in New York City, September 6, 1912.

BI-CALCIC PHOSPHATE PRODUCED BY ELECTROLYTIC ACID AND ALKALI.

By W. Palmaer.

In order to meet the ever-growing demand of agriculture for phosphate fertilizers, the following preparations are at present produced: Acid phosphate, basic slag, bone meal, bi-calcic phosphate. These are here named in the order corresponding to the amount produced, acid phosphate being the phosphate fertilizer most largely produced, its annual output amounting to about 10,000,000 tons.

Bi-calcic phosphate has so far been produced only in small quantities, the production in Germany and France, for instance, during 1900 amounting to about 5,000 tons for each country. To date this material has been obtained only as a by-product in the manufacture of glue, *i. e.*, in the process when bone is soaked in diluted hydrochloric acid, whereby the main product in the manufacture, the glue substance, remains undissolved, while a solution of bone phosphate is obtained as a by-product. This is turned to account by precipitation with lime, by which means bi-calcic phosphate is obtained.

On the other hand, it is a long while ago since it was first proposed to obtain bi-calcic phosphate as the chief product from every kind of raw phosphate in the same way, *viz.*, by extracting the raw phosphate with hydrochloric acid and precipitating the solution thus obtained with lime. This method would have the advantage that one could make use of very poor and otherwise valueless raw phosphate, provided it did not contain too large a proportion of any useless soluble compound, such as carbonate of lime. In the production of acid phosphate, on the other hand, one cannot utilize raw phosphate carrying a lower percentage than about 50 percent of bone phosphate, since, owing to the admixture of gypsum, the percentage of available phos-

phoric acid in the acid phosphate is only about half that in the raw phosphate, consequently consideration of freight charges for the prepared article excludes the use of a raw material in which the percentage is low.

However, it has been found that the price of hydrochloric acid has been too high for the adoption of this method. This in its turn is due to the fact that the production of hydrochloric acid according to the old methods entailed the sacrifice of sulphuric acid.

But the case is different if the acid is produced in such a way that a suitable salt, for instance perchlorate of sodium, is electrolyzed with a diaphragm, so that free acid is generated in the anode chamber, and a solution of caustic alkali in the cathode chamber. With an electrolyzing tension of 4½ volts and 80 percent current efficiency it is easy to calculate that in order to produce a kilogram-equivalent of acid, 182 horse-power-hours are required, whereby the alkali necessary for the precipitation of the bi-calcic phosphate is obtained at the same time without additional cost in the cathode chamber. If we assume that 1 electric horse-power can be obtained for $10 a year—the usual price in many parts of Europe and presumably in many places in America—then the cost of 1 kilogram-equivalent of acid amounts to about 24 cents, the alkali being obtained at the same time; while with the old method lime had to be purchased. There is no outlay for material beyond what is caused by spilling, etc., since the electrolyte regenerates itself, as will be seen from what follows.

If we assume that the price of 1 ton of chamber acid with 65 percent H_2SO_4 is $5.00, the cost of a kilogram-equivalent of H_2SO_4 (49 Kg.) is about 38 cents.

This calculation consequently shows that provided the remaining outlay for the electrolytic process can be kept within reasonable limits, it should be assured of success, especially as it allows of the utilization of otherwise valueless raw phosphate or refuse.

This calculation was the basis of my investigations, the object of which was consequently to try to make the method economically feasible, chiefly by finding a suitable electrolyte and by constructing a serviceable electrolyzer. As in the process there

is no consumption of chemicals, beyond loss by spilling, etc., the cost of the sulphuric acid used in producing acid phosphate is replaced by the cost of the electric power. The economic result of the process depends therefore in the first place on the price of the power.

General Features of the Process.

In an apparatus expressly constructed for the process, a solution of chlorate or perchlorate of sodium is electrolyzed. In the anode chamber an acid is thereby generated—chloric or perchloric acid—and in the cathode chamber a solution of caustic soda. The electrolysis is continued until a certain quantity of the dissolved salt has been separated into acid and alkali. The anode and the cathode solutions are led off into separate receivers. The acid anode solution is then allowed to work in dissolving tanks upon raw phosphate, in which process the phosphate is dissolved. Into the solution thus obtained, decanted from the dissolving tanks, the alkaline cathode solution is introduced, the whole meanwhile being kept vigorously stirred, until the liquid bears evidence of a slightly acid reaction; to obtain that result about half the cathode solution is required. In the reaction, bi-calcic phosphate is precipitated as a finely crystalline precipitate, which is drained off by filtration and washed. The filtrate, which contains one-third of the lime originally dissolved, but hardly any phosphoric acid, now has added to it the remainder of the cathode solution, which has previously been saturated with carbonic acid from fuel-gas. The lime is precipitated as carbonate, which is allowed to settle. The solution remaining above it is then drawn off. The original electrolyte is regenerated by use of this solution, and again enters the electrolyzing apparatus. Of course, the hydrogen obtained as a by-product at the cathode in the electrolysis of the salt solution could be used for making ammonia or in any other way, thus increasing the value of the products obtained.

The Nature of the Electrolyte.

With reference to the electrolyte, the salt used should be of such a nature that its acid may yield, in conjunction with lime, an easily soluble salt, and of a kind which is not subject to change during electrolysis.

As electrolytes, solutions of perchlorate of sodium or chlorate of sodium are suitable, or else mixtures of those salts, the presence in small quantities of other salts, for instance chlorides, being of no account. Both these salts can now, since they are being produced by electrolysis, be had at reasonable prices. Nitrate of sodium cannot be used, because it is too strongly reduced at the cathode to nitrite, ammonia, etc.

Perchlorate of sodium is an ideal electrolyte for the purpose in question. On electrolyzing its solution with a diaphragm, sodium hydrate is formed in the cathode chamber and perchloric acid in the anode chamber, while hydrogen is developed at the cathode and ozonized oxygen at the anode. No noticeable reduction of the salt occurs at the cathode, nor any other change, and the solution of perchloric acid obtained is perfectly constant at such temperatures as occur in the electrolysis (maximum 50° C.). Furthermore, the salt is exceedingly easily soluble (deliquescent) and thus easy to wash away.

Chlorate of sodium is less constant, in that the chloric acid solution formed in the anode chamber already begins to decompose at 40°C., free chlorine being developed. Moreover, it is considerably reduced at the cathode to chloride. But the principal change is that the development of oxygen at the anode almost ceases, because the chlorate is there oxidized to perchlorate. For this reason a start can very well be made with chlorate of sodium, since though the drawbacks mentioned (the decomposing of the chloric acid and the reduction of chlorate) appear at first, they disappear when the chlorate has become perchlorate of sodium. Even if one begins with chlorate of sodium, the electrolyte consists after a while of pure perchlorate, which, as has been said, suffers no further change.

The loss of perchlorate of sodium by spilling and incomplete washing need not, according to our experience, be estimated higher than at about 1 percent of the weight of the bi-calcic phosphate developed.

Another way of carrying out the process is this: A solution of chloride of sodium is electrolyzed so that a solution of caustic soda and free chlorine is obtained. The chlorine is transformed in the usual way into hydrochloric acid, wherewith the raw phosphate is dissolved, and a precipitate is formed by use of the

caustic soda. The salt is then regenerated as before. Although common salt is cheaper than perchlorate of sodium or chlorate of sodium, the process by several reasons (depreciation of anodes, losses of chlorine, etc.) is not so advantageous.

The Electrolysis.

The electrolysis of the perchlorate of sodium solution must be carried out, as has been mentioned, in a diaphragm apparatus, and it is clear that the problem is to find a suitable anode and a suitable diaphram. Both difficulties have been solved in a perfectly satisfactory manner, but for the present I cannot enter into details.

The voltage has been found to amount on the average to 4.5 volts per cell, including loss in connections. It varies somewhat, depending on the age of the diaphragm, the efficiency of the electrical contacts, and temperature of the solutions, which latter may vary at different times of the year; but, as stated, the average voltage is 4.5 The polarization amounts to 2.97 volts.

In a diaphragm process, where the new substances formed at the cathode and the anode remain in the solution (in this case alkali and perchloric acid), the current efficiency continually diminishes in proportion as the newly-formed substances begin to take part in the current-circuit. We generally produce solutions with 1 gram-equivalent of acid or alkali per liter, have a current efficiency of 82 percent, and a ballast of undecomposed salt in both acid and alkali solutions.

The Raw Material and its Utilization.

The high percentage raw phosphates used to make acid phosphate can be employed for the process, but it is not for such, but rather for low-percentage raw phosphates, at present worthless or of inferior value, that the process is primarily designed. Here I need mention in illustration only low-percentage apatites and apatite waste, waste from magnetic separation of phosphoric iron-ore, and certain low-percentage phosphorites.

As the process consists in dissolving the bone phosphate occurring in raw phosphate, and then precipitating bi-calcic phosphate from the solution, the product obtained will always be of the

same nature, irrespective of the percentage of the raw phosphate. We have employed raw products whose percentage of bone phosphate varied between 20 percent and 88 percent.

Furthermore, the raw phosphate need not be finely pulverized, provided that the bone phosphate is not embedded in insoluble minerals and that other soluble substances, such as certain silicates, do not occur in too great a quantity; we have worked with material as coarse as 5 cm.

Assuming that the solution of bone phosphate is effected according to the formula

$$Ca_3P_2O_8 + 6HClO_4 = 3Ca(ClO_4)_2.2H_3PO_4$$

then per liter of normal acid 23.7 grams of phosphoric acid should be dissolved. It can be foreseen, however, that the reaction, in contrast, for instance, to the reaction

$$CaCO_3 + 2HClO_4 = Ca(ClO_4)_2 + H_2O + CO_2$$

will not proceed quantitatively, since phosphoric acid is a much stronger acid than carbon dioxide. We have also found that we must reckon with a somewhat lower figure, say 20 gr. P_2O_5 or 43.6 gr. $Ca_3P_2O_8$ per liter of normal acid. This figure holds good provided that no other bodies soluble in acids occur in the raw phosphate.

Of such, in the first place, we must take into consideration calcium carbonate, for, as we know, it readily and completely dissolves in acids. As the equivalent weight for phosphoric acid (P_2O_5) is 23.7, and for carbon dioxide (CO_2) 22, we can consequently state that 1 percent of CO_2 in the raw phosphate causes approximately the same consumption of acid (or of energy) as 1 percent of P_2O_5, without giving any product of any value to speak of (the amount of carbonate of lime obtained as a by-product will, of course, be correspondingly greater). A raw phosphate which contains 20 percent of P_2O_5 (as $Ca_3P_2O_8$) and 2 per cent of CO_2 (as $CaCO_3$) consequently requires about 10 percent more energy than a raw phosphate with the same proportion of phosphoric acid, but free from carbonate of lime.

Iron oxides (iron-ores), on the other hand, are only dissolved very slightly. We found that after 24 hours' shaking at the

usual temperature with normal acid there was dissolved from magnetite a quantity corresponding to 0.24 gr. Fe_2O_3 per liter, from hematite a quantity corresponding to 0.20 gr. Fe_2O_3 per liter, which amounts are of no practical importance.

Most silicates are, as we know, insoluble in diluted acids. However, silicates may occur, for instance, together with apatite, which are so easily soluble that they dissolve to a noticeable degree if the acid is in contact with them for any length of time after most of the phosphate is dissolved. Attention must be paid to this in the course of the lixiviation, and the work regulated accordingly.

As regards the utilization of the bone phosphate in the raw material, we can as a rule count upon extracting 98 percent of it, sometimes more, sometimes a little less when easily soluble silicate, for instance, is present.

Precipitation of Bi-Calcic Phosphate and Calcium Carbonate.

To precipitate the bi-calcic phosphate we make use, as before stated, of the solution of caustic soda obtained by electrolysis.

The employment of the soda solution as a precipitant, instead of milk of lime, has a considerable advantage; for the fact is that as soon as the solution has become alkaline at any point bone phosphate is precipitated there instead of bi-calcic phosphate. This once-precipitated bone phosphate is only slowly converted into bi-calcic phosphate, even if the average acidity of the liquid is such that only bi-calcic phosphate ought to occur. At least a portion of the bone phosphate thus formed remains therefore in the precipitated bi-calcic phosphate. The bone phosphate thus precipitated is very finely distributed, it is true, and is even soluble after drying in 2 percent citric acid; but it has no fertilizing value worth speaking of. The phosphoric acid precipitated as bone phosphate must therefore be looked upon as lost.

Now it is clear that it is much easier to avoid the formation of bone phosphate if a sodium hydrate solution, distributed in jets, were employed as the precipitant, than if milk of lime were used, since in the latter case we get particles of solid calcic hydrate, around which the solution easily becomes alkaline.

Experience also proves that in employing sodium hydrate, which is added until the phosphate solution remains very slightly

acid or only just neutral, bi-calcic phosphate can be precipitated so completely that only 0.1 to 0.2 percent of all the phosphoric acid remains unprecipitated, while 98 percent of the phosphoric acid in the bi-calcic phosphate is soluble in citrate, and only 2 percent of the phosphoric acid is present as bone phosphate.

The precipitated bi-calcic phosphate, which is micro-crystalline, is filtered off, washed and dried. It thus forms a light, pure white powder, and its proportion of citrate-soluble phosphoric acid amounts to from 35 to 38 percent, according to the completeness of the drying.

If we call to mind that about 2 percent of the phosphoric acid in the raw phosphate is left behind in the extraction, that no quantity to speak of remains unprecipitated, and that about 2 percent is recovered as precipitated bone phosphate, we shall find that about 96 percent of all the phosphoric acid in the raw phosphate is extracted in the process as valuable citrate-soluble phosphoric acid.

The bi-calcic phosphate obtained shows, even if it contains iron and aluminum phosphate, no falling off in soluble phosphoric acid, which is simply due to the fact that it can be perfectly dried, after which no conversion can take place. On the other hand, as we know, deterioration shows itself in damp acid phosphate. The following analysis may be quoted to show that such degeneration does not occur:

	Total P_2O_5	Citrate-soluble P_2O_5	Citrate-soluble P_2O_5 in Percent of Total P_2O_5
Fresh	35.45	34.58	97.54
After three months	36.02	35.13	97.53
After six months	36.54	35.72	97.75

From the filtrate, after the bi-calcic phosphate is removed, the lime that remains in solution is precipitated by the remainder of the sodium hydrate solution, the latter having been saturated with carbonic acid from fuel-gases. The carbonate of lime precipitate can be used as a fertilizer or in chemical works. Its weight is about ¼ of the bi-calcic phosphate obtained, if the raw product used be free of carbonate. If calcium carbonate occurs in the raw product, the mass obtained in the process will be proportionately increased.

Power Consumption.

From the statements given above, it is easy to calculate what one electric horse-power (direct current) will produce per year of 8,400 hours. It works out to 2.24 tons of bi-calcic phosphate, with 35 percent of citrate-soluble phosphoric acid, if the raw material is free of carbonate. If a 38 percent article is produced,

$$\frac{2.24 + 35}{38} = 2.06$$

metric tons per horse-power year will be obtained, etc. The production with carbonaceous raw product has been stated above.

Value of Bi-Calcic Phosphate Fertilizer.

Careful experiments extending over many years have been made, partly by Professor H. G. Söderbaum, Agricultural Chemist at the Central Institute for Experimental Agriculture, Stockholm, partly by Dr. Hj. von Feilitzen, Director of the Swedish Peat Society, Jönköping, Sweden. Professor Söderbaum's earlier investigations are reported in "The Experiment Station Record," edited by the U. S. Department of Agriculture, Washington, Vol. XIV., No. 10, pp. 951-2 (1903), and he has also summed up the result of his investigations under the title of "Vegetationsversuche mit gefälltem Calcium-phosphate," in the "Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich," 1908, pp. 506-510. Dr. von Feilitzen has communicated the chief results of his investigations in the "Journal für Landwirtschaft," 1910, pp. 33-43.

As Dr. von Feilitzen is going to give an account of his further investigations at this Congress, I will here only briefly mention the chief result of his and Professor Söderbaum's cultivation experiments.

The result is, that the citrate-soluble phosphoric acid in the bi-calcic phosphate is proved to possess the same fertilizing value as the water-soluble phosphoric acid in the superphosphate, and consequently has the same value as a commercial product. That result might, indeed, have been foreseen, inasmuch as it is probable that the superphosphate in the soil is rapidly transformed into bi-calcic phosphate through the agency of the compounds of lime present there. This result is supported by the

tests carried out by practical agriculturists, who are well satisfied with both the result of the phosphate and its qualities in general. Owing to its high percentage, the freight charges are low for the valuable ingredient, and a very small amount need be manipulated by the farmer. It is in all other respects easy to handle and does not damage the shipping sacks in the least.

The Advantages of the Electrolytic Method.

The merits of the electrolytic method are as follows:

1. It admits of the use of cheap low-percentage raw phosphate which is not available for the superphosphate industry.

2. By it a phosphate containing 35 to 38 percent of soluble phosphoric acid is obtained, even from low-percentage raw material.

3. Freightage for a given quantity of phosphoric acid in the finished article is only about half that in the case of ordinary superphosphate.

4. Diminution or reversion of soluble phosphoric acid when stored does not occur.

5. The raw phosphate need not be reduced to a finely powdered state.

6. Bi-calcic phosphate can be employed as a fertilizer on all kinds of soil, even on sandy and boggy land.

7. Bi-calcic phosphate will be of excellent use in the manufacture of "complete fertilizers."

8. Sacks are in no wise damaged by the product.

9. The product is a finely divided, white powder, which is easily spread on the field.

The process is now being operated commercially. A small factory, the first one, has been put up by the Difosfat Company, at Trollhättan, Sweden, in the immediate vicinity of the Elektrotermiske Zinc Works and the Jernkontorets electric pig-iron furnace. Further developments on a large scale are expected in the near future.

Stockholm, Sweden,
September 1, 1912.

A paper presented at the XXII General Meeting of the American Electrochemical Society, in Joint Session with Sections VIa: Paper, and Xa: Electrochemistry, of the VIII International Congress of Applied Chemistry, in New York City, September 10, 1912. Prof. C. F. Burgess in the Chair.

RECENT PROGRESS IN THE ELECTROLYSIS OF ALKALINE SALTS.

(THE WILDERMAN CELL.)

By Dr. M. Wilderman.

Introduction.

In the following a short description of the Wilderman cell will be given, and its essential features, both technical and electrolytic, as distinguishing the same from all other mercury systems, will be given and explained, so as to give an idea of the progress thus made in the electrolysis of alkaline salts both from the practical and theoretical point of view. A large installation with the Wilderman cell has been put up at the Zellstoffabrik Waldhof, in Mannheim, Germany, for a production of 10,000 tons of bleach per annum, which has operated without interruption for about 16 months, and which is now being increased to a production of 14 to 15,000 tons of bleach per annum. The technical results given here are therefore not problematic; some of the first cells have been now working 19 months.

Description of the Cell.

In Fig. 1 a sketch is given to illustrate the construction and working of the Wilderman cell. It consists of a decomposing compartment *a* and of a combining compartment *b* which are separated by a partition composed of superimposed troughs which also has compartments containing mercury. *G* shows the anodes. The inner compartment *a* contains a saturated solution of sodium chloride or potassium chloride, the outer compartment *b* contains caustic soda or caustic potash of about 20 to 22 percent. The current is passing from the anode *G* through the brine to the mercury in the troughs, and from here back to the dynamo or to the next cell; alkaline metal is thus deposited by the current

on the surface of the mercury and forms immediately therewith an amalgam, while the chlorine is separated on the anode *G* and is conducted away for the production of bleaching powder or chlorates, etc. The teeth *T* of the stirrers *S* are dipping into the mercury of the troughs, so as to effectually mix the amalgam formed on the top surface of the mercury with the mercury beneath it.

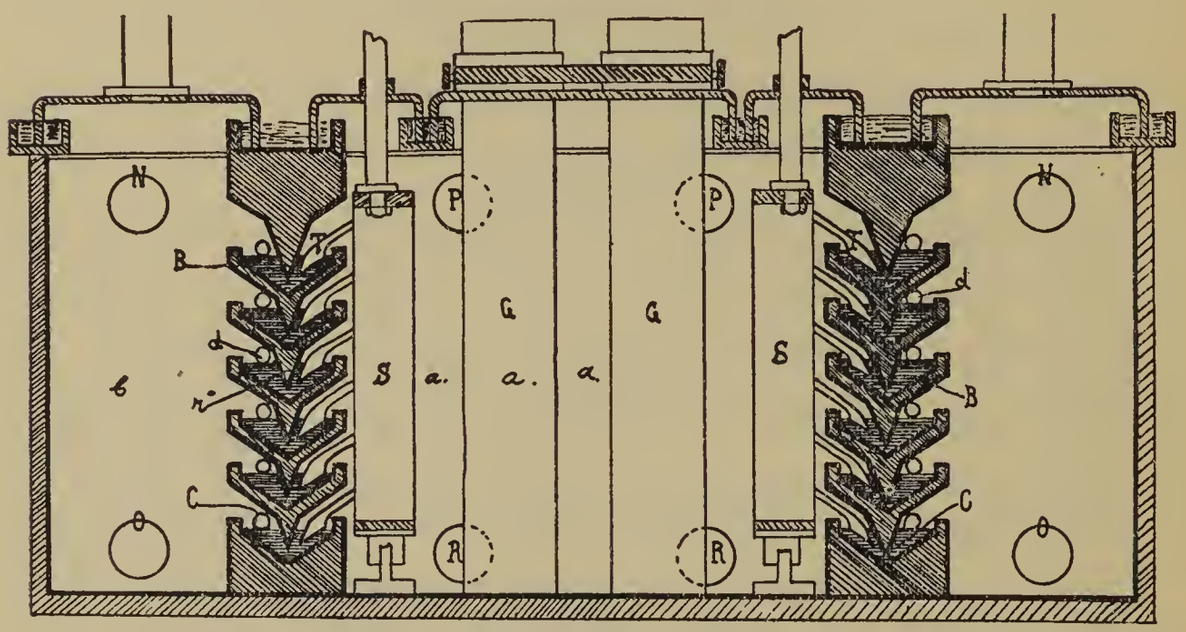


FIG. 1.

A special feature of the Wilderman cell is that in every and in all its parts it is built of iron covered with ebonite of Dr. Wilderman's invention, which stands both caustic and chlorine excellently. One millimeter of this ebonite stands about eight years' exposure to chlorine and is not affected by caustic at all. Through this I was able to build a cell which combines the strength of iron, as is requisite in the heavy chemical industry, with the chemical strength and life of the ebonite, and a cell was obtained which is capable of living 15 years or longer, and which practically requires no repairs.

Another special feature in the construction of the Wilderman cell is that the superimposed troughs can be put *ad libitum* far from one another, so that the surface of the anode is many times greater than that of the cathode. On this account the current density is very high upon the mercury surface but comparatively small on the anode surface, so that graphite anodes instead of

platinum electrodes can be used, and at the same time much greater current densities can be obtained with the same volts. This is not possible with the other cells where the anode is of necessity smaller but not larger than the cathode.

A third special feature of the Wilderman cell is that the mercury is placed in the vertical wall and not at the bottom of the cell and that it is supplied with stirrers which always keep the surface perfectly clean from dirt, which is important for the efficiency and the good work of the cell. All the dirt from the brine as well as the decomposed carbon settles at the bottom and not on the mercury. Contrary to this, all the dirt and decomposed carbon settle down in cells with horizontal mercury or horizontal diaphragm on the mercury or the diaphragm itself. The Wilderman cell has also no diaphragms to replace, so that there are no causes for interruption of its work. At the Zellstoffabrik Waldhof very cheap and inferior salt is used containing about 4 per-cent sulphates, calcium, magnesium, iron, slate, etc., and still the cell has to be cleaned only once in 6 to 8 months; with better salt it should work uninterruptedly for a year and longer.

Conveying of the Amalgam.

Instead of the amalgam remaining on the top surface of the mercury, as in other mercury systems, and leading here to the formation of strong or even of solid amalgams, the top layer of the mercury amalgam is stirred in the Wilderman cell by the stirrers dipping into the mercury. The mercury on the top surface is thus made comparatively dilute and the metallic sodium is uniformly distributed through the whole mass of the mercury on the chlorine side down to the lower rim of the trough *r*. At the same time the stirrers are also below the mercury on the caustic soda side. As the amalgam at the lower rim of the trough is lighter than the mercury on the top, on the caustic side which is practically free from sodium, the amalgam rises on the caustic side immediately from below the rim to the surface of the mercury by buoyancy. From the top surface of the mercury on the caustic side the sodium or potassium are removed with enormous rapidity by the small carbons *d*, which are in electrical contact with the amalgam, forming with it a local battery, so that the mercury on the top is practically free from sodium or

potassium. On this account it may be taken as approximately correct that the speed with which the amalgam rises from below the rim of the trough to the top surface of the mercury is directly proportional to the concentration of the amalgam below the rim of the trough or on the chlorine side.

Disadvantages of Older Mercury Systems.

In all other mercury cells the sodium entering the surface of the mercury remains in the top layer of the same, its thickness being perhaps only a small fraction of a millimeter, because the amalgam is lighter than mercury, while all the rest of the mercury below practically remains free from sodium. In all mercury cells there has to be provided a partition with a mercury seal between the decomposing and combining compartments in order that the liquids should not mix, and the bodily transportation of the amalgam always takes place through the mercury seal by some sort of mechanical means, be it by tilting of the whole vessel or by pumping or by siphoning, etc. During this transportation the poor amalgam from the lower layers of the mercury passes through the mercury seal first, while the rich amalgam from the top surface of the mercury remains to a great extent behind in the decomposing compartment, because a part of the mercury amalgam must be left back to preserve the mercury seal and to prevent the mixing of the liquors. This gradually leads to the formation of very rich and solid amalgam which is then skimmed off at the mercury seal and leads to a diminution of efficiency of the cell. Because of this we have in all mercury cells, where the amalgam is bodily transported from the decomposing compartment into the combining and *vice versa* the following technical conditions and principles as unavoidable; the amalgams formed must remain dilute, mobile so as to be able to transport them more easily to the decomposing compartment and so as to avoid as far as possible the formation of solid amalgam. On this account all these processes can work only with comparatively small current densities. The practice has shown in case of good mercury cells such as Castner or Solvay, that the suitable current densities are about 6 to 8 amperes per decimeter square of mercury and that as soon as higher current densities are tried they suffer from the formation of solid amalgams, eventually from

explosions owing to the decomposition of the amalgam and the formation of hydrogen with the chlorine, and such cells can also work only comparatively short periods without being stopped and cleaned (such a cell is known to me on the Continent).

The new principle of transportation of amalgam by buoyancy leads to very high current densities; it also makes the transportation self-regulating and independent of strict conditions of work; it makes the formation of solid amalgam impossible.

Contrary to the above we do not transport the amalgam bodily from the chlorine side to the caustic side in the Wilderman cell. The mercury on the caustic side is kept in the cell perfectly still and upon this depends to a very great extent the good efficiency of the cell and the purity of its products. The object of the stirrers is solely to make the amalgam on the chlorine side of a uniform concentration down to the lower rim of the trough, so as to keep on the one end the amalgam on the surface thin and to make on the other end the transportation of the amalgam to the top of the mercury surface on the caustic side by buoyancy possible and effective. This enables us to work with quite enormous current densities unknown and inaccessible before. The higher the current density employed the greater the concentration of the amalgam on the chlorine side and below the rim, and the greater is the speed with which the amalgam is brought by buoyancy from below the rim to the top surface of the mercury, and *vice versa,* this speed being, as explained above, directly proportional to the concentration of the amalgam below the rim or to the current density. The process of transportation is therefore in itself self-regulating and automatic and does not require any adaptation of working conditions to the current density employed, nor any special regulation or supervision of the amalgam; in fact the cell cannot be turned out of its normal work. At the Zellstoffabrik Waldhof, Mannheim, small cell units are used which occupy only three square meters floor area but work with 6,000 amperes each, the current densities being only 30 to 33 amperes per square decimeter of mercury. We are, however, able to work with current densities up to 60 and 70 amperes per square decimeter of mercury, almost up to the concentration of solid amalgam, without the least danger of formation of solid amalgam. Through such a cell, therefore, very

much more current can be sent, if electrical energy is cheap enough and if it pays to do so. The Wilderman cell is therefore to be characterized as a high-current-density cell, the highest possible for a mercury process, and as a cell which is self-regulating in actual running.

The following table gives the current density per square decimeter of mercury in the Wilderman cell, at different volts, at 70°C.:

Volts	3.93	4.32	4.72	5.11	5.5	5.89	6.28	7.06	7.85
Current density.	10	15	20	25	35	35	40	50	60

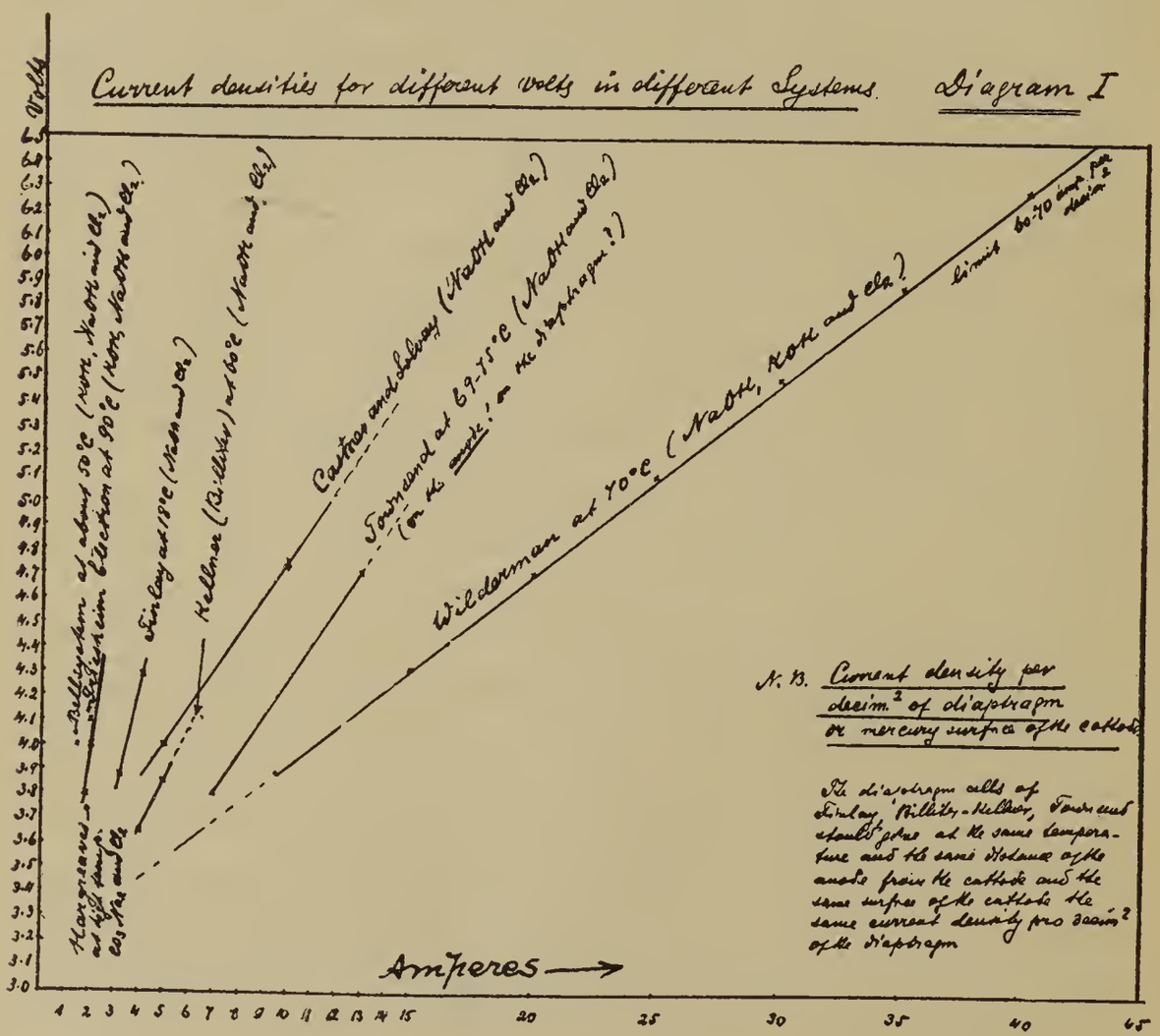

Current densities for different volts in different Systems. Diagram I
Volts
Amperes
Wilderman at 70°C (NaOH, H2O and Cl2)
limit 60-70 amp per dcim²
Kellner (Billiter) at 60°C (NaOH and Cl2)
Townsend at 69-71°C (NaOH and Cl2)
Castner and Solvay (NaOH and Cl2)
Hargreaves
Billiter-Leykam at about 30°C
Siemens Electron at 90°C
Solvay at 15°C (NaOH and Cl2)
N. B. Current density per dcim² of diaphragm or mercury surface of the cathode
The diaphragm cells of Solvay, Billiter-Kellner, Townsend and Castner also at the same temperature and the same distance of the anode from the cathode and the same surface of the cathode the same current density pro dcim² of the diaphragm

FIG. 2.

Fig. 2 gives the volts and current densities in the Wilderman cell and in other mercury and diaphragm cells. It is to be seen from the same: 1st, none of the others are able to get the same high current densities with the same volts; 2d, none of them are able to work with the same high current densities as the Wilderman cell.

What now are the important technical advantages of the high current densities and of the self-regulating properties peculiar to the Wilderman cell?

1. In the first instance we are able to work the power installation at its maximum capacity, that is most economically, the same cells taking up automatically all the energy the power installation is capable of supplying at any given moment.

2. The higher current density leads to higher efficiency, and to the practically total absence of hypochlorites.

When the current is passing from the anode to the cathode it decomposes the sodium chloride into metallic sodium and chlorine, the sodium entering into the mercury cathode surface and the chlorine separating on the anode. This is the electrolytic process of decomposition. At the same time, however, the two following chemical reactions tend to take place, and it is evident that upon low speed of these reactions depends the high efficiency of a given mercury system. The one reaction is, the sodium of the amalgam combines with water, giving caustic soda, and this, with chlorine, gives hypochlorites and chlorates, which destroy the anodes. The second reaction is the direct re-combination of chlorine with the sodium of the amalgam to sodium chloride. According to the laws of mass action in heterogeneous systems, the speed of these two reactions will be the slower the smaller the surface of the mercury in contact with the liquid and the smaller the concentration of the sodium in the top layer of the amalgam. In the Wilderman cell the concentration of the amalgam is made very small on the top surface by the stirrers, and as the current densities in the same are about five times as great as those of other good mercury cells, the surface of the mercury exposed to the liquid is for the same production therefore about one-fifth as great, and therefore the relative speed of the two chemical back reactions is correspondingly smaller. On this account the Wilderman cell is distinguished from other mercury cells both by a much higher efficiency and by smaller amounts of hypochlorites.

The efficiency of the Wilderman cell when specially attended to is 94 percent, the technical efficiency of the factory at the Zellstoffabrik Waldhof, owing to losses, is 90 to 92 percent for bleach and about 90 percent for caustic. The technical efficiency

of the Castner and Solvay apparatus is about 85 percent; of others is not certainly known to me. Fig. 3 gives the efficiency of different systems at different concentrations of the caustic, as given by the authors themselves. It will be seen that no mercury and no diaphragm system is capable of getting the efficiency of the Wilderman cell at the same concentration of the caustic, since in the diaphragm cells the efficiency drops very rapidly the higher the concentration of the caustic.

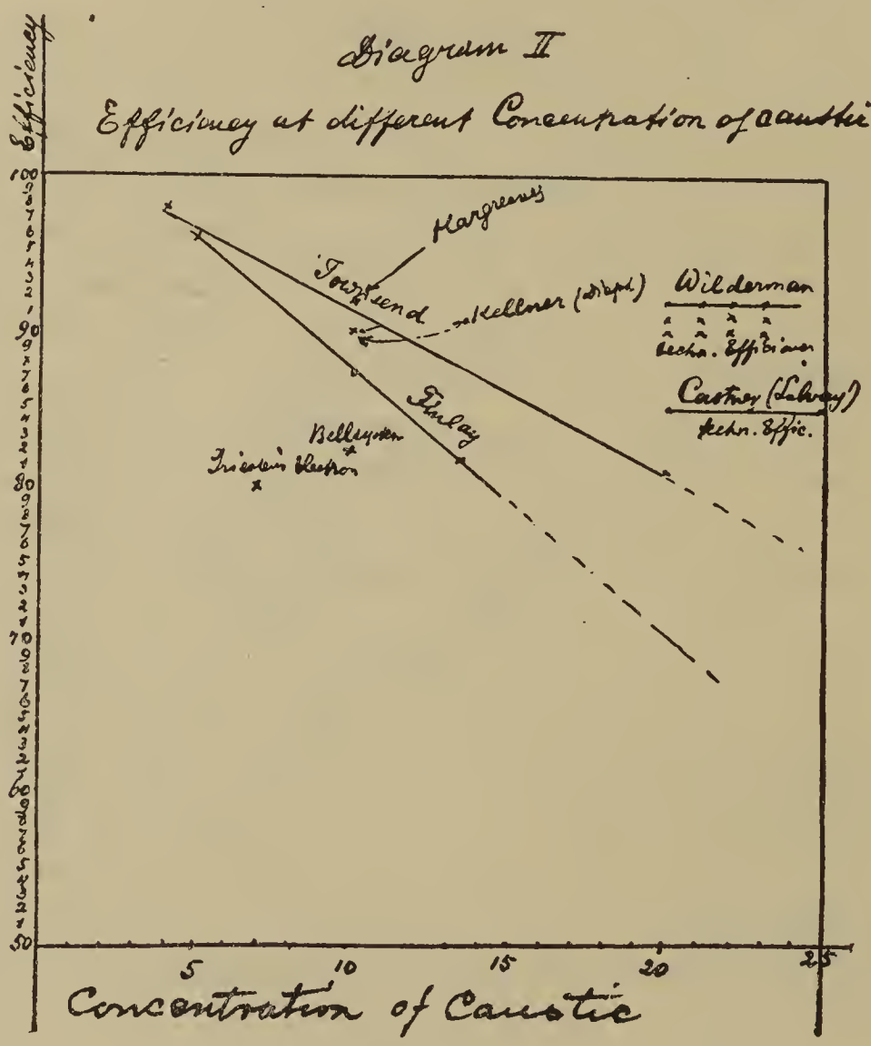


FIG. 3.

The amount of hypochlorites in the brine at the Zellstoffabrik Waldhof is only 0.02 to 0.04 percent and none in the caustic. As is known, other systems suffer from hypochlorites in the brine and a great number of diaphragm systems give also hypochlorites in the caustic. The first destroy the anodes, the second is injurious to the evaporating installation and to the melting pots. The amount of graphite requisite per ton of bleach is therefore con-

siderably smaller in the Wilderman cell than in those suffering from hypochlorites and using graphite anodes.

3. High current densities lead to great economy in the cost of the installation and in the cost of production.

High current densities mean small cells for large production. At the Zellstoffabrik Waldhof a small cell 3 square meters floor area works with 6,000 amperes; the whole production of 15,000 tons of bleach per annum requires only 80 cells. This means also that we require less land, less buildings, less foundations, less electrical conductors and anodes, less mercury and circulation pipes, less labor, etc. The whole building of the cell room for 15,000 tons of bleach is about 15 meters by 60 meters; we use about 80 gr. of mercury per ampere, where some of the best mercury systems working with siphoning and pumping use 250; we require only four men per shift to attend all the cells, for taking samples and for filling and emptying the same, and one man per shift to keep the cell-room clean; with the very bad salt we use we require for cleaning the cells four men per annum, counting together the whole time requisite for it; with better salt we should require correspondingly less; we use two men to attend the keeping good contacts in the whole installation, as we found that it paid to do so, and we hope to be able to reduce this labor as well. The small number of cells and their long period of work also means a great reduction in the losses of caustic and of mercury, and the high current density makes quite unnecessary the artificial heating of the cells by steam, which is unavoidable for cells with small current densities.

DISCUSSION.

MR. JASPER WHITING: I would like to ask Dr. Wilderman how he decomposes his amalgam in the oxidizing chamber, whether he depends on local action or other means?

DR. M. WILDERMAN: Local action; the carbon is in contact with the amalgam.

MR. A. H. HOOKER: In looking at that curve of the Townsend cell there seems to be about 3.7 volts at 5 amperes per square

decimeter, and the curve seems to run through the single point there. Isn't that a one-point curve?

Dr. Wilderman: Those are the figures given by Dr. Baekeland at the International Congress in London.

Mr. Hooker: But there are not two points on that curve.

Dr. Wilderman: Because you gave only two points. There are only two points there. We know how to draw a curve, you know. I have drawn more curves than you people during all your life, you know. (Laughter.)

Mr. Hooker: That is very possible.

A paper presented at the XXII General Meeting of the American Electrochemical Society, in Joint Session with Sections VIa: Paper, and Xa: Electrochemistry, of the VIII International Congress of Applied Chemistry, in New York City, September 10, 1912. Prof. C. F. Burgess in the Chair.

SOME FACTORS IN THE COST OF SODIUM HYPOCHLORITE PRODUCTION.

By Wm. H. Walker and Ralph Gegenheimer.

In the manufacture of bleaching liquor or sodium hypochlorite by the direct electrolysis of common salt the four most important factors entering into the final cost are labor, deterioration of apparatus, cost of salt consumed, and cost of power employed. Of these the first two, while important, are not subject to such variations incident to change in locality of the operation as are the last two, and are relatively constant. It is, therefore, to the relation of the cost of salt and cost of power as influenced by the conditions under which an apparatus may be operated that the present paper is devoted.

The experimental data employed were obtained from experiments made with an electrolyzing apparatus of the continuous-flow type. It consisted of a rectangular trough divided into twenty-four compartments by bi-polar electrodes of graphite. The salt solution to be decomposed was fed continuously into one end of the apparatus, passed successively between each pair of electrodes and removed at the opposite end. The electric current was supplied from a 110-volt lighting circuit, the amperes flowing depending upon the total resistance of the apparatus.

Since the salt solution as made up is used in its entirety for bleaching purposes however much or little of the salt therein contained may have been converted into the active bleaching agent, sodium hypochlorite (in any case there being always a large excess of unconverted salt) it is obvious that the less salt the solution contains per gallon the cheaper the resultant bleach solution will be. From this point of view, therefore, the apparatus should be fed with as dilute a solution of salt as will conduct the electric current through it. But on the other hand the more

dilute the salt solution is, that is, the less salt it contains per gallon, the more electrical power will be required to form a given amount of sodium hypochlorite in it. It becomes important therefore to consider the relationship which exists between the strength of salt solution used and the factors controlling the amount of electrical energy consumed per unit of sodium hypochlorite produced.

It can be shown that the cost of bleaching solution as measured by the cost of salt and electrical power consumed is influenced by a large number of factors, and that not infrequently the maintenance of one condition will influence the cost in opposite ways. Summing up these factors their relationship may be expressed in a general way as follows:

Increasing the amount of salt per gallon of salt solution used *increases* the total cost, because it:

1. Makes more expensive the first cost of the solution.
2. Causes a higher final temperature when there is heavy chlorate formation.
3. Increases the amount of current flowing and thus increases deterioration of electrodes.

It *decreases* the cost because it:

1. Lowers the resistance to the current and consumes less energy.
2. Decreases chlorate formation at the anode.
3. Increases production of cell.

A rapid rate of flow of solution *increases* final cost because it:

1. Increases the consumption of salt.

It *decreases* the cost because it:

1. Maintains a lower temperature, and prevents chlorate loss.
2. Maintains a lower hypochlorite concentration and prevents reduction at the cathode.
3. Lowers chlorate formation at the anode.

Increasing the amount of available chlorine per gallon of solution *increases* the final cost because it:

1. Increases the reduction loss at the cathode.

2. Increases the oxidation loss at the anode.

3. Increases the temperature of outflowing solution.

It greatly *decreases* the total cost, because it:

1. Makes more available chlorine per gallon of effluent, and hence reduces the number of gallons of solution required for a determined amount of available chlorine.

It is apparent from the above considerations that if we use a large amount of salt we will economize in electric power, and *vice versa*. The price which must be paid for salt and power varies at different localities, and the amounts of salt and power which are most economical at one place may be the wrong amounts to use at another place where the costs are different. The question arises, therefore, how can the relationship between the cost of salt and cost of power be established, and how can such relationships be most conveniently expressed in order to be of general use?

Obviously from the complicated relationship shown above it will be necessary to make a great many experiments if we are to learn in a quantitative way how variations in the several factors affect the result. The following method was therefore developed, by which from the data from one experiment a series of results may be calculated.

The apparatus was equipped with thermometers, and means of withdrawing samples for analysis in the 4th, 8th, 12th, 16th, 18th, 22d and end compartments. The run was commenced with a definite strength of salt solution, and the rate of flow was fixed to give a strong bleaching solution in the last compartment. The current was allowed to flow for an hour or so, or until the apparatus came to equilibrium. That is, until the flow of current and the flow of solution into and out of the apparatus was constant, the temperature of the different compartments did not change, and the strength of available chlorine in the last compartment was constant. At this point the temperature in each cell was read, and a sample of the solution was taken from each of the cells equipped for the purpose, that is, from 4, 8, 12, etc.

This sample and temperature represent the condition of the solution which would obtain if the apparatus ended with the

respective compartments. That is, suppose the apparatus ended with the 4th compartment, then the solution would leave it at this point and would have the temperature and composition of the sample taken from the compartment, when the current and rate of flow were as above given. This is true of the other compartments tested.

The complete data of such a run are given.

Run No. 20:

Sp. Gr. salt solution at 15°C. 1.0335 (= 0.4 lb. per gallon).
Average volts, 104.
Average amperes, 39.
Rate of flow, 11.5 gallons (52 liters) per hour.
Cost of salt per pound, 0.5 cent.
Cost of power per K. W. H., 2 cents.
Temp. inlet solution, 53.6°F. (12°C.).
Temp. outlet solution, 125.6°F. (52°C.).
Temp. rise, 72°F. (40°C.).

No. Cell	Temp. °F.	Lbs. Cl. per Gallon	Current Efficiency Percent	K.W. H. per lb. Cl.	Lbs. Salt per lb. Cl.	Cost Power	Cost Salt	Combined Salt and Power per lb. Avail Cl.
4	69.8	0.0178	60.5	2.44	22.5	0.0488	0.1125	0.1613
8	80.6	0.0294	50.2	2.94	13.6	0.0588	0.0680	0.1268
12	95.	0.0418	47.5	3.11	9.57	0.0622	0.0479	0.1101
16	107.6	0.0492	41.9	3.52	8.14	0.0704	0.0407	0.1111
19	114.8	0.0529	38.0	3.88	7.56	0.0776	0.0378	0.1154
22	125.6	0.0563	34.9	4.23	7.12	0.0846	0.0356	0.1202
End	126.5	0.0574	32.6	4.52	6.97	0.0904	0.0349	0.1253

This table shows in the first column how the temperature of the solution increased as it passed through the apparatus; the second indicates the way in which the available chlorine is increased as measured in pounds per gallon. The third column gives the percentage of the current passing through which has been utilized in making the desired product, and it is seen to fall off as the end of the apparatus is reached. The power consumed per pound of available chlorine produced therefrom increases, while the amount of salt used per pound of available chlorine decreases as the solution becomes stronger in its bleaching power. This is true also of the cost of the two elements.

Following the explanation above given we see that if the apparatus ended with the 4th compartment, and was fed with salt solution containing four-tenths pound per gallon, at the rate of 11.5 gallons per hour, a current of 29 amperes would pass through, and the outflowing bleach liquor would be at a temperature of 69.8°F., and would contain 0.0178 lb. of available chlorine per gallon. The current efficiency would be 60.5 percent and the total cost per pound of available chlorine provided would be 0.1613 cent. If the apparatus ended with the 12th compartment the table shows the values which would here be obtained, and so on.

It is seen therefore, that under the conditions of cost of salt and power, strength of salt solution and rate of flow as here obtaining, it would be cheapest to stop the operation at the 12th compartment, where the available chlorine produced cost $0.1101 per pound. Beyond this point, as the solution passes through the apparatus more hypochlorite is formed, but the expenditure for power is large, owing to chlorate formation and cathode reduction, as compared to the saving in salt, and the net cost of available chlorine produced becomes larger as we pass beyond the 12th compartment.

But since the apparatus is of 24 compartments designed to operate on a current of 110 volts, in order to use an apparatus of the size represented by the 12th compartment we would require a generator furnishing twelve twenty-fourths of 110 volts, or 55 volts. Since we are *limited* to a current of 110 volts, it simply becomes necessary to use two such 12-compartment apparatus in series, if we wish to get the advantages indicated. Each of these apparatus would be fed with the same strength brine at the same rate, and the result would be that we would get the same results of minimum cost in both pieces of apparatus, use the entire voltage of the line, and produce twice as many gallons of bleaching solution.

Now practically this same result may be accomplished if we used the original 24-compartment apparatus with the 110 volt current, and run the salt solution through *twice as fast* as in the experimental run. While the additional rate of flow would of course maintain a lower temperature, and hence a somewhat

smaller number of amperes would flow through the apparatus, the loss of hypochlorite through reduction would be greater, inasmuch as that made in the first compartment is subjected to the cathodes of the following compartments, and the concentration of the hypochlorite would also increase more slowly and hence the loss would be correspondingly smaller.

Hence if by such an experimental run it is found that available chlorine can be produced cheaper after the solution has passed through any given number of compartments, N, at the rate of flow of R gallons per minute, the rate X at which the solution must flow through the entire 24 compartments of the apparatus to get the same cost per pound is given by the proportion:

N	:	*24*	.=	*R*	:	*X*
The number of compartments in experimental run giving minimum cost.		The entire apparatus.		The rate of flow during experimental run.		The required rate of flow throughentire apparatus.

To test the validity of this method two runs were made with a 5 percent brine, one at the rate of 35 liters per hour and another at 70 liters per hour. According to the above reasoning the results obtained at cell No. 12 in the first run should be the same, within the limits of experimental error, as the results at the end of the apparatus when the rate is twice as fast. The following values were obtained:

	Results at Compartment No. 12	Results at End of Apparatus
Rate of flow liters per hour	35	70
Grams chlorine per liter	3.7	3.8
Temp. Rise	15°C	15°C
Current efficiency	45.6%	46.8%
Cost per kg. Chlorine	$0.270	$0.271

The figures show a satisfactory check.

Cost Ratio.—The combined cost of salt and power may be expressed as a ratio of one to the other. Thus if the cost of power per K. W. H. is 2 cents and the cost of salt is 0.5 cent per pound, the ratio is 2 divided by 0.5, or 4. That is, power is four times as expensive as salt in their respective units. By taking one of

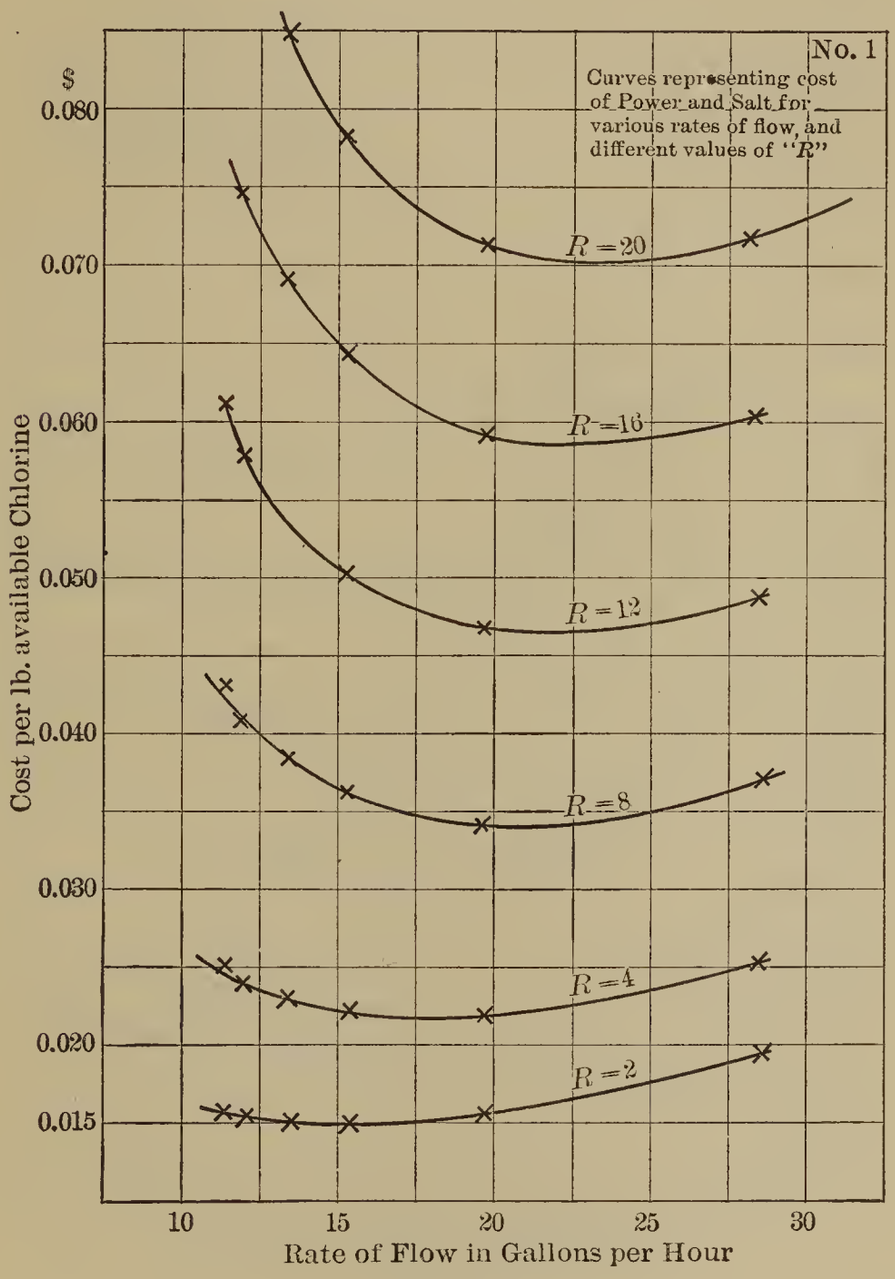


FIG. 1.

these factors as unity, we may construct a table showing the relation between the rate of flow of any given brine through the apparatus and the combined cost at any ratio of cost of salt to cost of power. This is given on Fig. 1 for a 10 percent salt solution, or about 91 pounds per 100 gallons. The cost figures

are based on salt at 0.1 cent per pound. Thus the bottom curve labeled R = 2 means when power costs twice as much as salt. If salt costs one-tenth cent per pound, the relation between rate of flow and cost may be read off directly; but if salt is 0.5 cent per pound (which would mean that power is 1 cent per K. W. H.,

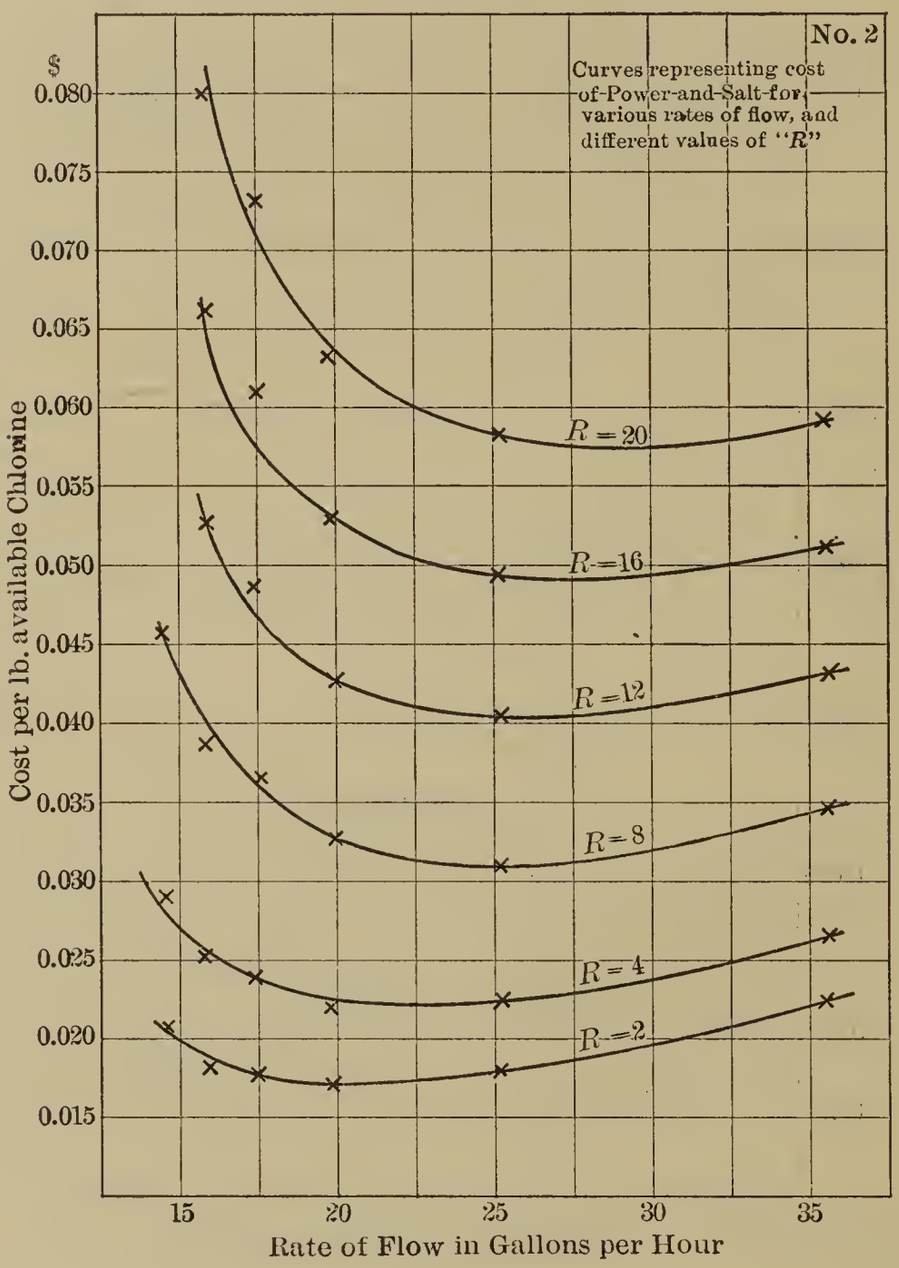


FIG. 2.

since the ratio is 2) the combined cost would be just five times the figures given as ordinates. Suppose we have a locality where salt is 0.3 cent per pound and power is 3.6 cents per K. W. H., this is a ratio of 12. Looking at the curve marked R = 12 we find that the lowest cost is at a rate of 25.5 gallons per hour.

The cost corresponding to this is 0.041 dollar. But this figure is for salt at 0.1 cent per pound. Since at the locality in question salt is 0.3 cent per pound the cost would be three times this $0.123, or 12.3 cents per pound of available chlorine. In a similar way we find from Fig. 2 for a 5 percent brine the

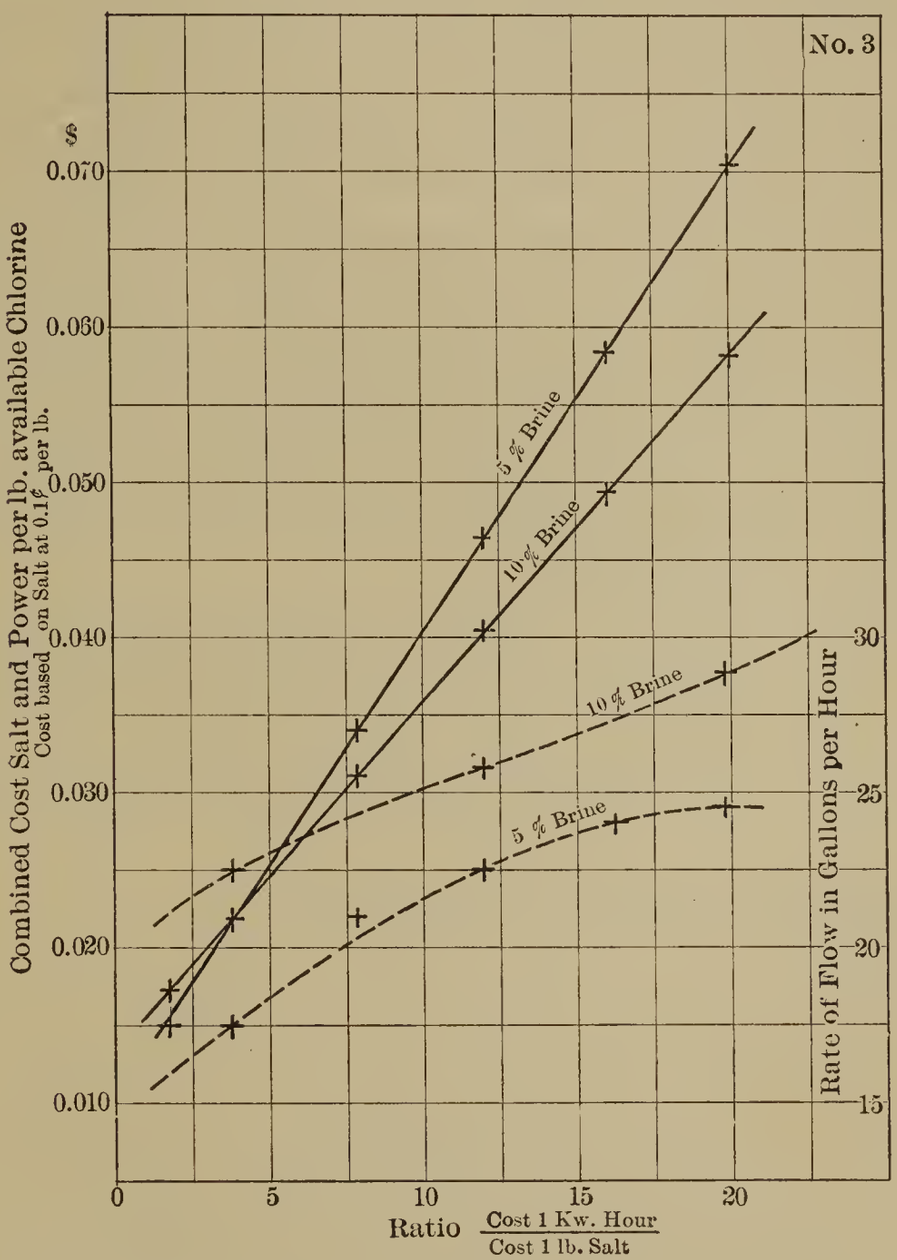


FIG. 3.

rate of flow showing the minimum cost is 22.5 gallons, and the combined cost is $0.138.

By combining the minimum cost points of all three curves and the corresponding rates of flow we have produced Fig. 3, which contains the final working curves. The solid curves

show the minimum combined cost based as before on 0.1 cent per pound of salt, in its relation to R, the ratio of cost of power per K. W. H. to cost of salt per pound. The dotted curves show the mean rate of flow to produce the minimum cost for the 5 percent and 10 percent brine.

The solid curves cross each other at a ratio of about 4. This means that in general where power is less than four times as expensive as salt it is cheaper to use a 5 percent brine or about 40 pounds salt per 100 gallons; otherwise a higher concentration up to 90 or 100 pounds salt per 100 gallons is cheaper. If the cost of power is much greater than twenty times that of the salt an apparatus of the type used here is inadvisable, since it will not run much faster than 30 gallons per hour at best. In this connection it must be mentioned that, although the cost for salt and power using a 10 percent brine is lower where R is greater than 4, the current density is considerably higher with the more concentrated solution and the cost for renewal of electrodes would be greater.

Such curves as these are all that are necessary to determine the strength of brine and the rate of flow which it is advisable to use in any particular locality with an apparatus of the type here used, to obtain a minimum cost for available chlorine, as soon as the costs of salt and power are known for that locality.

Massachusetts Institute of Technology,
Boston.

DISCUSSION.

PROF. C. F. BURGESS: The discussion of this paper is in order. May I ask Dr. Walker if there are practical conditions in which it would be preferable to develop hypochlorite this way rather than by bleaching powder and sodium carbonate—the chemical method of producing the hypochlorite?

DR. W. H. WALKER: I am unable to state the relative value of the two methods of making sodium hypochlorite, but from the fact that a number of such pieces of apparatus as this are being

sold I should judge that under certain conditions the electrolytic method was preferable.

MR. M. L. GRIFFIN: I have known a few bleacheries and laundries which have employed this device with very satisfactory results. They have usually taken current from their lighting circuit and made no account of its cost. It is not claimed that it is less expensive, but a more active agent for their uses that solutions of bleaching powder, and more convenient.

Chemicking with sodium hypochlorite leaves the goods softer, and is found to produce softer effects in mercerized yarns and piece goods, and avoids the use of undesirable softeners.

DR. W. LASH MILLER: One use, I think, is sure to be made of Dr. Walker's paper. In more and more colleges there is coming to be a course on electrochemistry given to engineering students, and the lecturer in charge is compelled to refer to the cost side, because that is what settles it, whether an electrochemical or other process will be used. Of all the refinements which the lecturers hunt up for that purpose I do not think there is one like that which Prof. Walker supplies us with. I think the lecture will become a regular classic in the teaching of the schools.

MR. H. P. BISHOP: I would like to ask Dr. Walker if it is possible to get free chlorine in that solution.

DR. WALKER: No, I do not think it is. Theoretically it certainly is not, because one is liberating at the cathode just the right amount of alkali to combine with the chlorine at the anode, and these electrodes are quite close together, not more than half an inch apart, so that the hydrogen which is evolved at the cathode causes an efficient mixing, and the two compounds are brought into intimate contact immediately. I think that chlorine is absent.

MR. GRIFFIN: One question I would like to ask Dr. Walker is whether or not he has had any experience in making the brine alkaline to influence the formation of chlorates, and perhaps make a product which would act as a cleanser from the alkaline side as well as a chemic at the same time.

DR. WALKER: We carried on a series of experiments with the hope of decreasing the formation of chlorate by maintaining

an alkaline reaction, but the net result was not satisfactory. As a matter of fact, in dilute salt solutions chlorate is formed directly at the anode, and is not a secondary reaction as is generally supposed. In saturated salt solutions this anode formation is negligible. An alkaline reaction does, however, render the solution of sodium hypochlorite much more stable.

MR. L. D. VORCE: It appears to me that Dr. Walker has made a demonstration that all laundry people are going to consult. They will not use the electrolytic process. They have to buy certain things anyway. They have to buy their salt, and the assumption is that they have to buy current. They have the apparatus to keep up, which may be simple, but, if like most electrolytic apparatus, requires considerable expert attention. The cost per pound of hypochlorite formed is considerably in excess of what it will cost to make the hypochlorite through the purchase and use of caustic soda and liquid chlorine.

A paper read before Section Xa: "Electrochemistry" of the Eighth International Congress of Applied Chemistry, in New York City, September 11, 1912.

PHYSICAL AND CHEMICAL DATA ON DRY CELLS AND DRY CELL MATERIAL.

By Carl Hambuechen and O. E. Ruhoff.

In the discussion of a paper on "Dry Batteries" presented recently before the Faraday Society, it was stated as noteworthy that the best of American cells are inferior to the best British types. Without going into the justice of this assertion, perhaps a presentation of some of the characteristics of typical American dry cells may be appropriate at this time. In presenting this paper the writers are indebted to the courtesy of the Northern Chemical Engineering Laboratories and the French Battery and Carbon Company, of Madison, Wisconsin, for permission to publish the following data obtained through a comparative study of various typical American cells.

A nearly standard method of construction appears to prevail in this country. The anode is a cylinder of sheet zinc, which serves also as the container. The electrolyte is a solution of zinc chloride and ammonium chloride held in a layer of absorbent material, usually paper, lying next to the zinc, and separating it completely from the cathode. The cathode consists of a carbon pencil surrounded by a granular mixture of manganese dioxide, carbon and ammonium chloride. Graphite is also a common ingredient. This granular mixture is saturated with electrolyte containing ammonium chloride and zinc chloride in solution.

Testing of Battery Materials.

The chemical inspection of dry cell materials should include a determination of the purity of these materials, especially as regards the presence or absence of quantities of useless inert substances, so as to indicate the percentage of the materials on which depend the usefulness of the cells. In addition to this,

tests should also be made for comparatively small quantities of such impurities as exert an actively injurious effect upon the cell.

The physical properties of some of the materials are of quite as great importance as are the chemical ones. One of the most important of these is the conductivity of the crushed carbon and graphite, and that of the mixtures of these materials with manganese dioxide. The conductivities of crushed carbon and graphite depend upon the raw materials used in their manufacture, the conditions of heat treatment used, and the size of the granules in the composition.

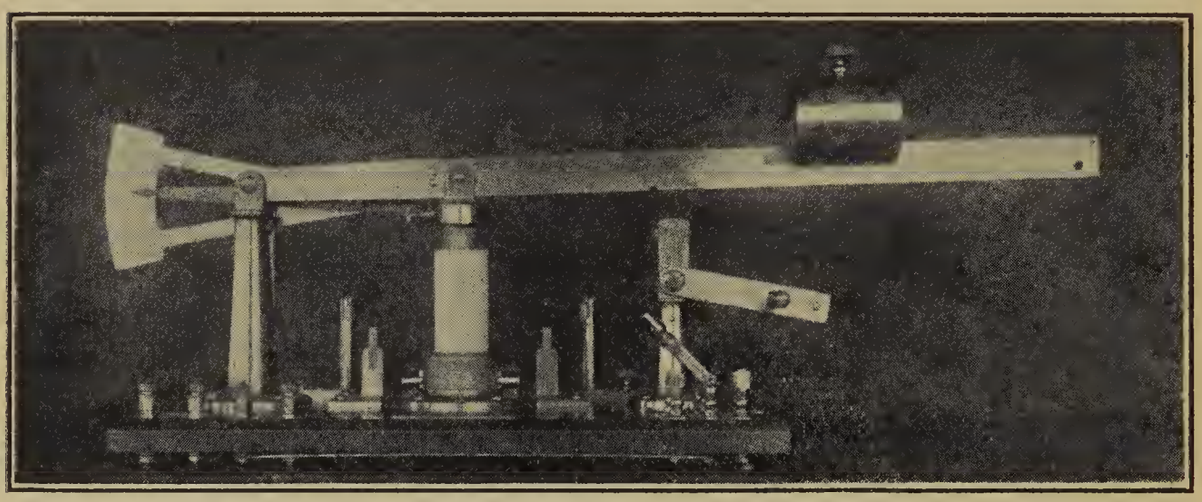


FIG. 1.

Battery carbon may be prepared from petroleum coke, retort carbon, or coke made from soft coal. The graphite which is used may be either a natural product or that manufactured by electric furnace methods. Crushed carbon and graphite may also be prepared from used furnace electrodes, or from worn out electrodes from electrolytic processes.

For the determination of the conductivities of crushed materials and mixtures, an apparatus especially devised for the purpose and shown in Fig. 1 was used. The material to be tested is placed in a porcelain tube 2 in. (5 cm.) long and 1 in. (2.5 cm.) inside diameter. The bottom of the tube is closed during the test by a removable graphite plug, and the tube is filled flush with the material to be tested. The tube is placed in an upright position and another graphite plug inserted at the top upon which a

pressure of 15 pounds (6.8 kg.) is exerted, by means of a suitably arranged lever and weight. A current of one ampere is passed, the graphite plugs serving to make connection to the column of granular material. The circuit includes an ammeter and a variable external resistance. The drop in voltage between the graphite plugs is measured by a voltmeter of suitable range. If accurately checking readings are desired, great care must be taken in the manner of applying the pressure to the tube full of granular material. This same testing apparatus is also arranged to test the conductivity and breaking strength of carbon pencils.

A number of samples of crushed graphite and carbon as supplied by various manufacturers and made by various processes have been tested for conductivity. For graphite there have been obtained readings varying between 0.071 and 0.411 ohm and for carbon between 0.188 and 0.637 ohm per linear inch (2.5 cm.) of a column one inch (2.5 cm.) in diameter, equaling resistivities of 0.14 to 0.82 ohm for graphite and 0.37 to 1.27 ohm for carbon, per cub. cm. The minimum readings in each case represent a very high grade of material, while the maximum ones indicate materials which are practically useless for most battery purposes. Most of the samples of carbon tested have been crushed so as to pass through about a 20 mesh screen (8 openings per cm.) while the samples of graphite will usually pass through a 100 mesh screen (40 openings per cm.).

In comparison with carbon and graphite, the other insoluble ingredient of pulverized dry-battery filler—manganese dioxide—has a very low conductivity, so that as far as the final conductivity of the whole mixture is concerned, the manganese dioxide may be considered as practically a non-conductor. It follows, therefore, that the higher the proportion of MnO_2 in the depolarizing mixture, as compared with the conducting ingredients, the higher will be its resistance, presuming, of course, that the size of granules in the composition and the quality of materials remains the same. The curves plotted on the accompanying chart indicate in a general way how the conductivities change with variations in the proportions of conductive to non-conductive materials, and with variations of the size of granules in the composition for the same proportions by weight. Variations in the con-

ductivity of ten to several hundred percent can be brought about by varying the size of granules in the composition of a mixture, with no change in the proportion by weight of the several ingredients.

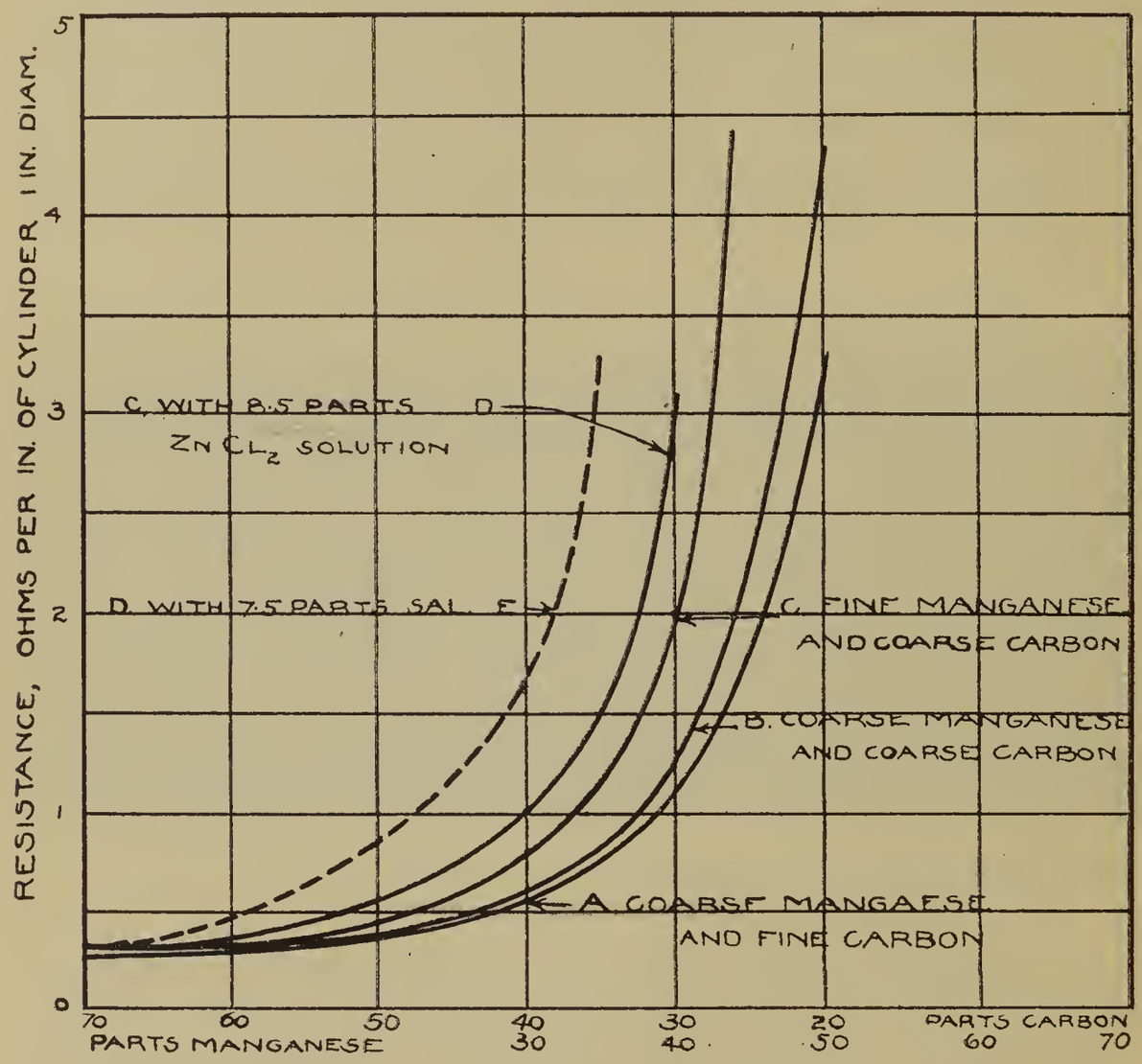


FIG. 2.

Inspection of Various Types of Cells.

Four of the typical brands of cells investigated and concerning which data are given in the tables are designated by the letters *A, B, C* and *D*.

It will be noted from the tables that there is comparatively little variation in the composition of these several makes of batteries. Perhaps one reason for this is the strong demand of the American market for a low-priced cell, compliance with which places narrow limits on the manufacturer in indulging any desire

he may have to improve the quality of the battery by using more expensive materials, or by devising a more complicated structure.

Table I shows the weights, dimensions and physical properties of several types of batteries. The size of granules in the composition and the percentage of MnO_2 on the several sizes of the washed and dried mixtures is shown in Table II. In general, it seems that an increase of MnO_2 in the coarser sizes will reduce the internal resistance of the battery. On the other hand there are indications that an increase in the proportion of very finely divided manganese dioxide results in greater depolarizing power per unit weight of the MnO_2.

TABLE I.

	A	*B*	*C*	*D*
Voltage of cell	1.50	1.57	1.55	1.50
Amperes on short circuit (flash test..)	33	33	32	30
Weight of cell, grams	980	932	984	942
Weight of moist depolarizing mixture, grams	642	545	576	574
Weight of paper lining, wet, grams	61	71	65	72
Diameter of carbon pencil { inches	1	1	1	0.75
Diameter of carbon pencil { centimeters	2.5	2.5	2.5	1.9
Weight of zinc, grams	117	110	132	151
Resistance, in ohms, of depolarizing mixture per linear inch of a 1-inch column	0.94	1.69	1.90	0.86
Resistance, in ohms, of depolarizing mixture per cubic centimeter (resistivity)	1.84	3.31	3.72	1.69
Relative coherence of depolarizing mixture	1.9	1.7	1.5	1.6

TABLE II.

Screen Analysis of Washed and Dried Depolarizing Mixtures.

	A	*B*	*C*	*D*
On 20 mesh (8 openings per cm.), percent	4.8	0.2	1.3	0.5
" 40 " (16 " " "), "	25.5	12.8	20.0	29.0
" 60 " (24 " " "), "	11.8	14.3	10.5	12.0
" 80 " (32 " " "), "	4.3	5.3	7.0	3.3
" 100 " (40 " " "), "	9.8	22.5	28.8	12.0
" 150 " (60 " " "), "	2.3	7.3	8.5	4.5
Through 150 " (60 " " "), "	41.5	37.6	24.2	38.7

Table III shows the quantities of zinc chloride and ammonium chloride present in the solution held in the paper, and in the solution with which the depolarizing mixture is moistened.

The quantity of water present in a No. 6 dry cell varies somewhat for different makes. The lower and upper limits are about 60 and 90 grams. Other things being equal, a better cell probably

results from approaching the latter figure rather than from too close an approach of the former.

Measurements of the conductivity of the mixtures were made directly upon the depolarizing material as removed from the batteries, but previous to making the test all of the mixtures were passed through a 10 mesh (4 openings per cm.) screen. The internal resistance of the battery depends, naturally, not only on the conductivity of the mixture but also the tightness with which it has been compressed in filling the cell. Additional factors influencing the internal resistance that will result from any given mixture are the weight per unit volume of battery space and also the manner in which the packing is performed.

TABLE III.

Percentage of MnO_2 in Various Sizes.

	A	*B*	*C*	*D*
On 20 and 40 mesh (8 and 16 openings per cm.)	74.9	71.5	82.5	60.3
" 60 " 80 " (24 " 32 " " ")	53.8	61.6	46.3	45.9
" 100 " (40 " " ")	45.2	38.3	27.1	41.8
" 150 " (60 " " ")	44.4	37.0	30.8	38.1
Through 150 " (60 " " ")	31.3	38.3	50.2	31.7

TABLE IV.

NH_4Cl and $ZnCl_2$ in Papers and Mixture.

	A	*B*	*C*	*D*
Grams NH_4Cl in papers, per cell	10.1	13.4	12.3	12.3
" NH_4Cl in mixture, " "	36.2	42.6	25.1	30.5
" NH_4Cl, total " "	46.3	56.0	37.4	42.8
" $ZnCl_2$ in papers, " "	7.0	6.8	9.7	8.9
" $ZnCl_2$ in mixture, " "	13.8	10.3	15.8	15.5
" $ZnCl_2$, total " "	20.8	17.1	25.5	24.4

The remaining common ingredient of dry cells is the least costly of all, but it is nevertheless of considerable importance. This is the air occupying the "void" spaces in the depolarizing mixture, that is, space not occupied by water, salts, carbon, graphite or manganese dioxide. The volume of voids varies from about 3 to 15 cubic centimeters. All of the data given have reference to a standard "No. 6" cell, the dimensions of which are 2.5 by 6 in. (6.5 x 15 cm.).

Northern Chemical Engineering Laboratories,
Madison, Wisconsin.

A paper read before Section Xa: "Electrochemistry" of the Eighth International Congress of Applied Chemistry, in New York City, September 6, 1912.

SYNTHESIS OF HYDROCARBONS AT HIGH TEMPERATURES AND PRESSURES.

By J. N. Pring and D. M. Fairlie.

The systematic study of a number of chemical reactions at high gaseous pressures, in a specially constructed electric furnace, was first carried out by Hutton and Petavel (Phil. Trans. London, A. **207**, 428 (1908). Such reactions were studied as the formation of calcium carbide, silicon carbide, the reduction of alumina by carbon, the fusion of silica, and the synthesis of oxides of nitrogen. Temperatures up to about 3000°C. were used, and pressures up to 200 atmospheres.

The present paper deals with a detailed investigation which has been conducted by the authors on the synthesis of hydrocarbons at high temperatures and pressures. The apparatus constructed for this work is a modified form of the pressure furnace used by Hutton and Petavel.

The investigation, which was carried out at temperatures and pressures which were carefully measured and controlled, was directed mainly to the determination of the quantities of methane which are in equilibrium with carbon and hydrogen at different temperatures. In this way it has been possible to obtain data which will correlate the values for the specific heats of hydrogen, methane, and different forms of carbon at high temperatures. The influence of temperature on the displacement of the equilibrium constant of a chemical reaction is a function of the heat change which accompanies the reaction at that particular temperature, while the heat of reaction itself changes with the temperature according to the specific heats of the substances taking part in the equilibrium.

The dependence of a chemical equilibrium on the various heat changes involved in the reaction has been pointed out by van't

Hoff, and further developed by Nernst and Haber, but there are very few cases where sufficiently accurate data are available to verify the application of these formulae at high temperatures.

In all cases when substances in a condensed system interact chemically, the reaction proceeds until a certain equilibrium stage is reached, when further action ceases, though in many cases the equilibrium stage is so far developed in one direction that the reaction appears to be complete.

At low temperatures, equilibrium values are often of very little importance, since under these conditions the rate of chemical reaction is usually so slow that the equilibrium value is never reached and does not come into question. At high temperatures, however, the conditions are usually quite different, the final equilibrium stage being more quickly reached, so that usually chemical changes do not complete themselves, but proceed to a certain stage, at which point the same proportion between the substances taking part, and the products of the reaction is obtained from whichever side the equilibrium is approached. At low temperatures many substances are in an unstable or "metastable" condition though they undergo no apparent change on standing, but at high temperatures this is not possible, as the change into the stable form proceeds with a velocity which continually increases with the temperature.

The reactions which have been investigated in this work, *viz.*, the synthesis of hydrocarbons, involve the case of interaction of a solid with a gas. In the case of each hydrocarbon a certain equilibrium stage is reached when the particular hydrocarbon bears a definite ratio to the quantity of hydrogen present. The quantity of carbon does not come into consideration in this equilibrium, since its active mass does not vary under different conditions.

As methane is an exothermic compound, it follows that the equilibrium amount decreases with increase of temperature. Below 1,000°, carbon and hydrogen at atmospheric pressure unite so slowly, even when the former is in presence of a catalyser like platinum, that equilibrium in the yield of methane cannot be reached in any reasonable time.

The velocity is considerably increased at high temperatures,

but even in this case it was not found practicable to determine the equilibrium value with methane below about 1,100°.

Above this temperature this synthesis was accomplished and measurements taken by heating carbon in the form of a rod in presence of hydrogen. The heating was affected by the passage of an electric current through the rod, which was thus the only part of the apparatus heated. The containing walls of the steel vessel were cooled by water.

Since methane is more stable the lower the temperature, it follows that the quantity of this hydrocarbon finally yielded will correspond to the equilibrium at the temperature of the heated carbon, since no decomposition could occur in passing to the colder regions of the apparatus. A large amount of work has been carried out by the present authors[1] on the synthesis of hydrocarbons at atmospheric pressure, and it has been found that traces of ethylene are also formed at 1,300° and above, but the quantity does not reach any considerable magnitude below 1,500° (at 1,400° the quantity in equilibrium at atmospheric pressure is about 0.005 percent).

The ethylene will react rapidly with the hydrogen in the cooler parts of the vessel, giving methane and thus gradually raising the quantity of the latter above the equilibrium value at the high temperature.

However, it was calculated that in the short time necessary to produce equilibrium with methane in these experiments at high pressures this disturbance would not reach any appreciable magnitude when working below 1,500°.

With regard to the synthesis of acetylene, it was found in the earlier work cited above that this first becomes noticeable (about 0.001 percent) at 1,650°, and the amount produced increases with the temperature, in accordance with the fact of it being an endothermic compound.

However, it has not been possible to determine the precise equilibrium values with acetylene, on account of the non-uniform temperature of the interior of the reaction vessel, which causes decomposition of the gas (produced at the high temperature of the carbon) to take place in regions of lower temperature. More-

[1] Pring and Hutton, Trans. Chem. Soc. (London), **89**, 1591 (1906); Pring, *ibid.*, **97**, 498 (1910); Pring and Fairlie, *ibid.*, **99**, 1796 (1911); **101**, 91 (1912).

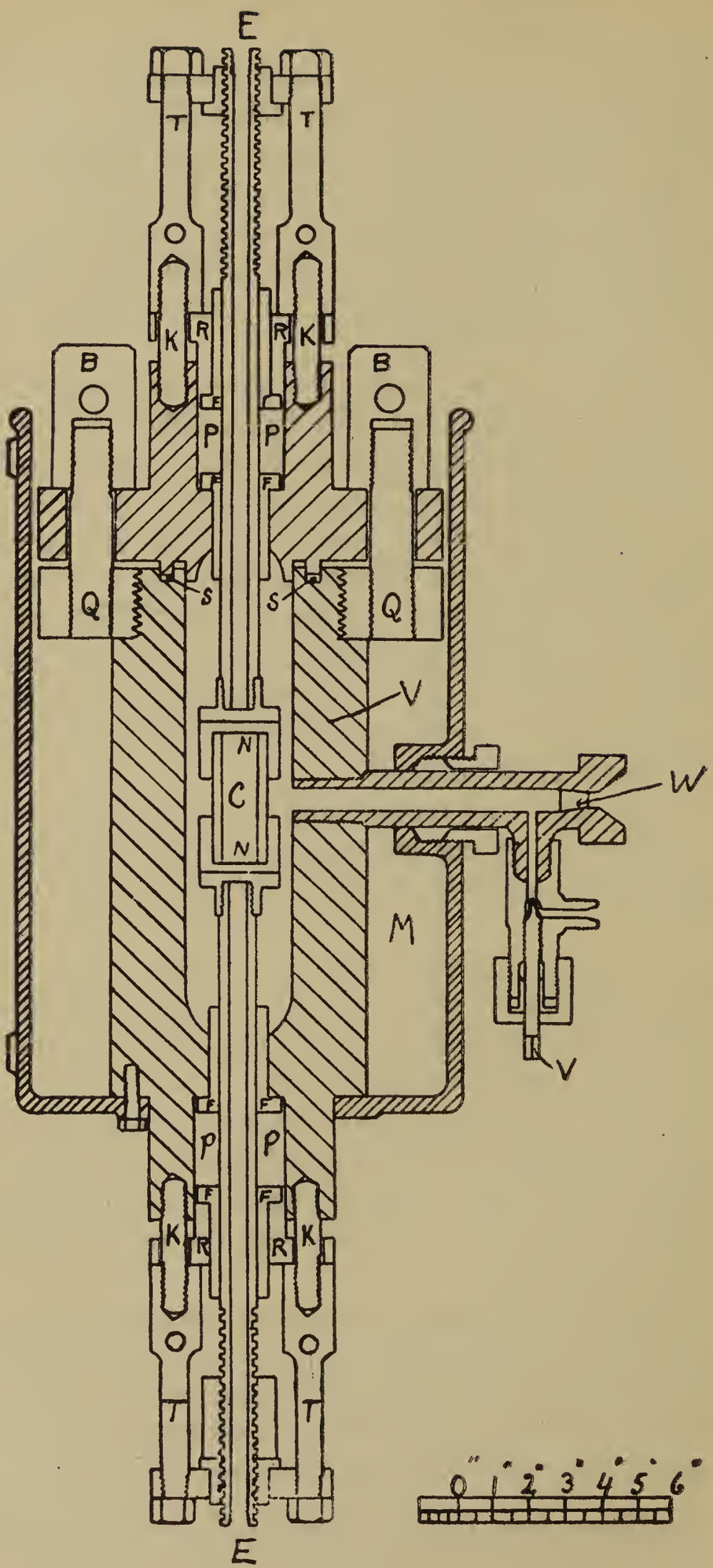


FIG. 1.

over at temperatures where the quantity of acetylene attains any considerable magnitude an exact estimation of the methane equilibrium is no longer possible, on account of the rapid combination of the acetylene with hydrogen, giving methane in the cooler parts of the vessel. For this reason it has been found possible in this work to measure with any accuracy only the equilibrium with methane, and that only in the range of temperature between 1,100° and 1,500°, though the experiments were extended up to 2,100°. It has been shown, moreover, that in this range, and at pressures up to 200 atmospheres, no hydrocarbons other than methane, ethylene, and acetylene are formed or can exist in any detectable quantity.

Considering the synthesis of methane, since the equilibrium is expressed by the equation $C + 2H_2 = CH_4$ it follows in accordance with the law of mass action that

$$\frac{p.\,CH_4}{p.\,(H_2)^2} = K$$

or the concentration of methane divided by the square of that of the hydrogen is a constant at any particular temperature. It follows from this that an increase of the pressure n times will increase the ratio of methane to hydrogen n times.

A proof that definite equilibrium values are obtained lies in the fact that the same final quantity of methane results in whichever direction the reaction is made to proceed, and further that the same value is obtained for K, the equilibrium constant, whatever gaseous pressures are employed.

Description of Apparatus.

The pressure cylinder V (Fig. 1) was forged from a piece of nickel steel of high tensile strength. The steel tubes $E\,E$ which served to lead in the current were cooled by water circulation, and contact with the carbon was made by means of nickel clamps $N\,N$, which were brazed to the ends of these leads. The arrangement in the diagram shows provision for heating larger carbon tubes, in which crucibles could be placed, but for the present purpose tubes or rods of carbon longer and narrower than the one shown in the diagram were used. These rods or tubes C

were always fitted in graphite end-pieces, which were held in the nickel clamps. The steel tubes emerged from the furnace at the stuffing boxes *P P* and were insulated from the walls by means of small tubes of ebonite or fibre *F F*. Asbestos cord mixed with a little tallow was used as the packing material for the boxes *P P*, and was compressed by the brass rings *R R*, which were forced down onto the ebonite tubes by 6 bolts, as at *K K*. The outward thrust of the electrodes was secured by the bolts *T T*, of which there were two at each end of the furnace. The top part of the furnace was fastened down by 6 bolts as at *B B*, and a gas-tight joint made by means of the lead spigot *S S*. By opening the bottom stuffing box and removing the packing the bottom electrode could be lifted while clamped to the carbon rod, which was also held in the top electrode. The two electrodes and the carbon tube could thus be all lowered into position together with the furnace top, and afterwards raised in the same manner. Water circulation was provided in the annular jacket *M*. The gas was admitted through the valve *V*, and the pressure read directly on a gauge. The glass window *W* was placed at a sufficient distance to be protected from the heat of the carbon. Temperature readings were taken by means of a Wanner optical pyrometer, from the light radiated by the carbon, after passing through the window and being reflected from a mirror placed in front at an angle of 45°. By comparing these indications with a thermo-junction, it has been found that there was no appreciable deviation at 1,300°, so that graphite must radiate approximately like the theoretical "black body." Measurements were made from time to time of the error arising from the absorption by the window and mirror. At 1,400° this usually amounted to about 60°. The absorption at any other temperature can be calculated from the formula

$$\frac{I}{T_1} - \frac{I}{T_2} = C$$

where T_1 is the real temperature, T_2 the apparent temperature after the absorption, and C is a constant for any given sample of glass.[2]

[2] Pring, Lab. Exercises in Phys. Chemistry, page 151. Manchester University Press.

The window could as a rule be safely used with pressures up to 200 atmospheres, and the remainder of the furnace was capable of withstanding a pressure of 1,000 at.

The carbon used at *C* consisted in some cases of the amorphous retort variety in the form of tubes 12 cm. long and either 20 mm. external and 15 mm. internal, or 15 mm. external and 9 mm. internal diameter.

With the small size, a current of 500 amperes, at 27 volts, would raise the temperature to 1,600°, when using hydrogen at 150 at. pressure.

In other experiments, rods of (Acheson) graphite 12 cm. long and 9 mm. diam. were used.

In the case of amorphous carbon not given a preliminary purification, before placing in the furnace, a partial purification was obtained by heating to about 1,400° in hydrogen at about 50 at. pressure, and then liberating and renewing the gas.

The quantity of combined hydrogen present as impurity in the carbon was always well below the amount of methane subsequently synthesized. The capacity of the furnace was about 750 c.c. A number of experiments at lower pressures were carried out with rods of amorphous carbon, 5 to 7 mm. diam. and 12 cm. long, which had been carefully purified by heating electrically in chlorine in a glass vessel to about 1,500° for a few hours, and then in hydrogen in the same manner.

On account of the corrosion of the carbon, it was not as a rule possible to use the same rod or tube in more than one experiment. In the course of a large amount of work, where carbon rods and tubes have been heated at atmospheric pressure under different conditions, it has been found that the heating, in the case of amorphous carbon, always takes place with great uniformity throughout the whole length and up to the cooled points of support. This is due to the negative temperature coefficient of resistance which causes a greater expenditure of electrical energy in places which tend to become cooler. With graphite, however, the temperature falls near the cold ends at the supports.

Preparation of Materials.

Hydrogen.—Electrolytic hydrogen was obtained commercially in steel bottles at a pressure of 120 at. On analysis, it was found

to contain 0.2 percent of nitrogen, and no appreciable quantity of other impurity. After admitting the gas to the furnace, the heating of the carbon enabled the pressure to be raised to 200 at.

Carbon.—Different varieties of carbon were used, as explained above, and in some cases were first purified by heating to a high temperature in an atmosphere of chlorine.

In some experiments carbon was used in presence of platinum or palladium, to act as a catalyser. For this purpose a layer of the metal was obtained by electrodeposition from a chloride solution.

Methane.—In some experiments an atmosphere of methane was admitted to the previously evacuated furnace, before filling in the hydrogen at high pressure. The hydrocarbon for this purpose was prepared by decomposing commercial aluminium carbide with water, washing the gas with ammoniacal cuprous chloride to remove acetylene and hydrogen sulphide, and then liquefying by means of liquid air. After evaporation, the gas was collected over water in a large holder of 20 liters capacity.

Analysis of Gases.

The gas obtained in these experiments, which contained from 1 to 20 percent methane, was analyzed in the Sodeau apparatus. By shaking the gas with an ammoniacal silver nitrate solution, acetylene (if present) was completely, and ethylene partly, absorbed. The remainder of the ethylene could then be removed by means of bromine. Carbon monoxide was then taken out by shaking with a freshly prepared solution of ammoniacal cuprous chloride. The hydrogen was then removed by mixing with an excess of oxygen and passing a few times over palladium sponge maintained at about 80° in a water bath.[3]

The saturated hydrocarbon could then be identified and estimated by the relation found between the contraction after combustion with oxygen, and the volume of carbon dioxide formed, as ascertained by absorption with potassium hydrate solution. In all these cases methane was at all temperatures found to be the only saturated hydrocarbon produced.

In an experiment carried out at 1,275°, an examination was

[3] Compare Pring and Fairlie, Trans. Chem. Soc. (London), **99**, 1796 (1911).

made for traces of ethylene by circulating a large quantity of the gas (25 liters) through a tube cooled in liquid air. Most of the methane was thus condensed, together with practically the whole of any ethylene present, as the latter has a higher boiling point than methane. This liquid was then allowed to evaporate slowly, and the last portion was passed through a tube containing carefully purified cocoanut charcoal, which had previously been heated for some time at a red-heat in a high vacuum. The gas absorbed by the charcoal in this experiment was then removed in fractions by evacuating. The last portion of 50 c.c. was analyzed and found to contain 0.51 c.c. of ethylene or 0.002 percent of the total gas, while the amount of methane in this particular sample was 21 percent. The ratio of ethylene to methane is lower than that found in earlier work at atmospheric pressure, and the ratio of ethylene to hydrogen is higher. This result is in agreement with the effect which would be expected theoretically from the influence of pressure on the yield of the different hydrocarbons.

Change of Pressure.

The formation of methane, proceeding according to the equation $C + 2H_2 = CH_4$, is accompanied by a contraction of volume equivalent to the volume of methane formed. In these experiments at constant volume this was equivalent to a change of pressure.

Consequently, by reading the pressure indicated by the gauge the course of the reaction could usually be followed, and the attainment of equilibrium recognized. However a considerable time was usually necessary for the mean temperature of the enclosure to become constant on account of the large quantity of metal present. Samples of gas were usually withdrawn at two or more different periods during the experiment, in order to ascertain when equilibrium had been reached.

The results of all experiments which were completed are tabulated below according to the particular variety of carbon, and in order of the temperature used.

As follows from the unstable nature of amorphous carbon, it was found that this modification gradually changed into graphite during the experiments in which it was heated at temperatures

above 1,100°, in presence of hydrogen. This change took place more rapidly the higher the temperature. It was found that the amorphous carbon which had been purified by heating to a high temperature in chlorine and then hydrogen was always more or less graphitised.

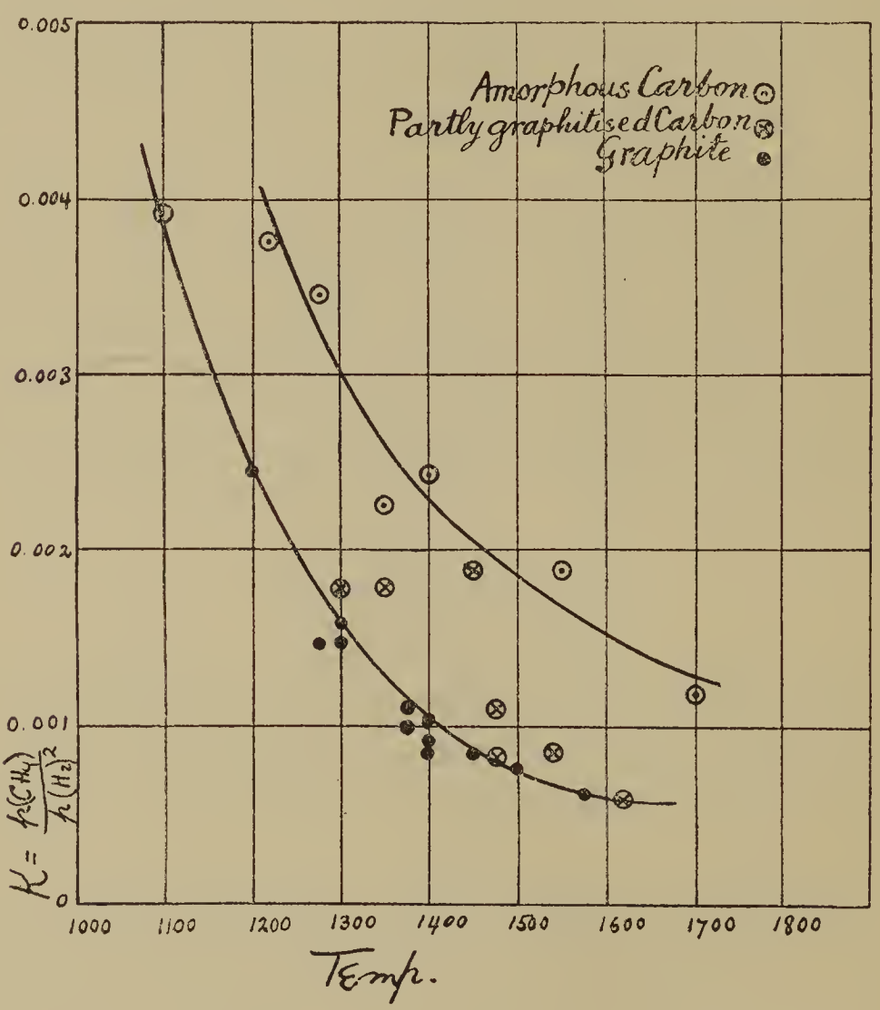


FIG. 2.

Amorphous carbon was found to give a considerably higher percentage of methane than graphite, and on beginning an experiment with amorphous carbon, the yield of methane which was at first obtained gradually fell concomitantly with the change of amorphous carbon into graphite. The increased yield of methane with amorphous carbon is in excess of the stable equilibrium value, and thus denotes a false or metastable equilibrium. This is only possible to such a degree on account of the great

inertness of methane, or the slow rate at which it breaks down into carbon and hydrogen.

These false equilibrium values with amorphous carbon have also been noticed by Schenck and Heller,[4] who studied the equilibrium in some reactions in which carbon in different modifications takes part.

In the case of the equilibrium between carbon dioxide, carbon monoxide and carbon, the reduction of the first was greatest when amorphous carbon was used.

A similar result was obtained in the reaction between iron oxide and carbon, thus in this case, at 550°, the pressure of the latter when in "metastable" equilibrium was, with amorphous carbon, 59 mm.; with diamond, 22 mm.; and the stable equilibrium value with graphite was 12 mm.

In the present work the results with amorphous carbon are given in Table I. In some cases the carbon was impure (though containing less total hydrogen than the quantity of methane subsequently formed); in others, it was partly purified in chlorine at a temperature too low to cause any appreciable change into graphite. In all cases the results given in this table refer to carbon which was used for the first time. In Table II are given the results of experiments carried out with graphite. This was either Acheson graphite or else carbon which had been used in a previous experiment and heated for a long interval at a high temperature in hydrogen, or else it had been purified at a high temperature in chlorine so as to cause transformation into graphite. The carbon in all these cases was practically pure.

In Table III are given the results of experiments with carbon which by previous heating or purification had become partly transformed into graphite. In some cases a thin layer of platinum or palladium was plated on the carbon by electrodeposition, as explained above, to serve as a catalyser. These cases are pointed out in the first column of the tables.

The general results are also plotted in the form of curves (Fig. 2), where the ordinates denote the equilibrium constants and the abscissae the temperatures. The only values which are quite definite are those obtained with graphite. In the case of

[4] Ber. Berichte, 38, 2139 (1905).

amorphous carbon, a continuous change in the methane yield followed the graphitization of the carbon. The whole of the results are entered in Fig. 2, though a number of the experiments in the case of graphite were not taken quite to the equilibrium point, so that the curve has been drawn through the maximum values.

TABLE I.

Amorphous Carbon. Used First Time.

Nature of Carbon	Temp. °C	Time	Pressure (at)	Percentage Composition				$K = \frac{p.CH_4}{p.(H_2)^2}$
				CO	CH_4	C_2H_2	C_2H_4	
Purified Pt. Coated	1100	0	.....	.....	4.10	.....	.....	.....
		2½ hrs	20	1.1	6.35	.....	.....	0.00390
Impure Pt. Coated	1220	0	.....	.....	4.1	.....	.....	.....
		3 hrs.	18	1.4	5.6	.....	.....	0.00376
Partly Purified.....	1275	3 hrs.	100	0.25	21.5	.....	0 002	0.00359
Impure Pt. Coated	1350	1 hr.	166	0.6	18.5	.....	.....	0.00173
		2½ hrs	153	0.7	20.9	.....	.....	0.00224
Purified Pt. Coated	1400	0	.....	.....	4.35	.....	.....	.....
		1¾ hrs.	18	0.92	3.86	.....	.....	0.00245
Same Carbon as above (To show effect of progressive graphitisation)	1400	1½ hrs.	19	1.0	2.35	.....	.....	0.00138
		3 hrs.	18.5	1.4	1.98	.....	.....	0.00120
		4½ hrs.	17.5	3.3	1.28	.....	.....	0.00084
Impure	1550	0	.....	.....	4.65	.....	.....	.....
		1½ hrs.	21	1.5	3.49	.....	.....	0.00188
Impure	1620	20 min.	20	3.7	1.0	.....	.....	0.00058
Impure Pt. Coated	1700	1 hr.	15	7.5	1 4	nil	.....	0.00120
Impure	1775	4 hrs.	117	1.6	9.0	nil	0.1	.....
Impure	1950	7 min.	24.5	3.4	2 4	0.29	0.44	.....
Impure	2050	7 min.	23	2.8	2 8	0.74	1.10	.....
Purified.....	2100	0	.....	.....	5.5	.....	.....	.....
		15 min.	25	5.5	2 6	0.25	?	.....

The values obtained in experiments above about 1,700° do not represent equilibrium, as the methane in these cases is formed chiefly by the reaction of ethylene and acetylene with hydrogen in the cooler parts of the vessel. The results at these higher temperatures are consequently not plotted in the figure.

TABLE II.

Graphite.

Nature of Graphite	Temp. °C	Time	Pressure (at)	Percentage Comp. of Gas		$K = \frac{p.CH_4}{p.(H_2)^2}$
				CO	CH_4	
Acheson	1200	2½ hrs.	105	0.0	17.5	0.00244
Carbon graphitised by heating. Pt. coated	1275	0	...	...	2.38	...
		25 min.	37	1.6	4.23	0.00133
		1¾ hrs.	32	2.4	4.02	0.00147
Carbon graphitised by heating. Pd. coated	1300	½ hr.	37	0.6	4.69	0.00120
		1 hr.	35.5	1.0	4.55	0.00146
Acheson	1300	1 hr.	117	0.0	11.2	0.00126
		2¼ hrs.	106	0.0	12.6	0.00158
Carbon graphitised by heating	1375	1 hr.	28	1.4	2.5	0.00100
Acheson	1375	3 hrs.	115	0.2	10.6	0.00117
Graphitised by heating. Pd. coated	1400	0	...	...	2.4	...
		¼ hr.	46	0.1	3.90	0.000945
		1¼ hrs.	46	0.2	4.29	0.00103
Graphitised by heating Pt. coated	1400	0	...	...	1.6	...
		1½ hrs.	50	1.3	3.99	0.00089
Same Carbon as above	1400	0	...	...	1.6	...
		¾ hr.	55	0.5	4.24	0.00080
		1¾ hrs.	48	1.0	3.71	0.00089
Carbon graphitised by heating. Pt. coated	1450	0	...	...	2.3	...
		20 min.	47	2.0	3.39	0.000843
		1 hr.	44	2.4	3 01	0.000746
Carbon graphitised by heating. Pt. coated	1500	0	...	...	1.8	...
		½ hr.	55	0.8	3.96	0.00080
		1 hr.	52	1.2	3.62	0.00077
Carbon graphitised by heating. Pt. coated	1575	0	...	...	...	...
		12 min.	52	0.7	2.94	0.00063
		1½ hrs.	44	1.0	2.46	0.00062

CONCLUSIONS.

The reaction between carbon and hydrogen resulting in the formation of methane was found to proceed with increased velocity at high gaseous pressures. Using carbon in the form of a compact rod or tube, and either in presence or absence of a catalyser, the equilibrium stage was reached in about 2 hours, when

the temperature was 1,200° to 1,300°, and the pressure 30 to 50 at. Above 1,400°, equilibrium was reached in about 15 minutes under the same conditions. At 200 at. the reaction was still more rapid.

TABLE III.

Partly Graphitized Carbon.

Nature of Carbon	Temp. °C.	Time Hours	Pressure (At.)	Percentage Composition of Gas		$K = \frac{p.CH_4}{p.(H_2)^2}$
				CO	CH_4	
Purified	1300	1¾	7	7·3	1.0	0.00178
Impure Pt. coated	1350	2	11.5	5.75	1.71	0.00178
Purified Pt. coated	1450	1¼	136	0.3	17.1	0.00186
Impure Pt. coated	1475	1¼	177	0.3	16.7	0.00137
		4½	155	0.3	11.9	0.00101
Impure	1475	1¼	200	0.05	13.1	0.00087
		3¼	200	0.25	12.4	0.00083
Impure . . .	1540	1½	183	0.05	12.0	0.00086

The results indicate the probability that carbon in a fine state of division would at still higher pressures combine with hydrogen with extreme rapidity, as the action is exothermic. In this way the preparation of methane, though necessarily present with a small percentage of hydrogen, might most conveniently be carried out on a large scale.

The relative amount of methane produced increases with the pressure to the extent demanded by the law of mass action as applied to the reaction $C + 2H_2 = CH_4$. According to this the value of

$$\frac{p.(CH_4)}{p.(H_2)^2}$$

should be constant at any given temperature.

In all experiments, at pressures varying from 10 to 200 at., a value which was constant within the limits of experimental error was always obtained for this ratio at any particular temperature, and when the same modification of carbon was used. In some experiments, where an amount of methane in excess of this value was added to the gas beforehand, decomposition took place until the same final value was obtained. Consequently this represents the true equilibrium constant.

The amount of methane which at atmospheric pressure is in equilibrium with hydrogen and graphite is at 1,200° equal to 0.24 percent, and at 1,500°, 0.07 percent. For amorphous carbon, the "metastable" equilibrium values are 0.36 percent at 1,200° and 0.18 percent at 1,500°. At a pressure of n atmospheres, the ratio of methane is n times as great as at 1 atmosphere.

The values found in this work for the equilibrium constants in the case of carbon and graphite enable an approximate calculation to be made of the heat of reaction in the transformation of amorphous carbon into graphite. According to Berthelot,[5] at ordinary temperatures this has the value 2,840 cal. per gram atom. This value at first falls with increase of temperature and at some temperature below 1,000° becomes zero. Consequently amorphous carbon is the stable form at this temperature, but not at ordinary temperatures. When heated above this stable point it again becomes unstable, and consequently passes more or less rapidly into graphite with evolution of heat.

The heat evolved in this transformation at different temperatures can be calculated by means of a formula deduced by van't Hoff. In this

$$Q_{(t)} = RT\ ln.\ \frac{K_{(1)}}{K_{(2)}}$$

Where $Q_{(t)}$ is the heat of reaction at the absolute temperature T, R the gas constant in calories (1.98), $K_{(1)}$ the equilibrium constant in the methane formula with amorphous carbon, and $K_{(2)}$ that with graphite. We have from the above results the following values for the heat of the transformation at different temperatures.

Temperature Centigrade	Temperature Absolute	$K_{(1)}$	$K_{(2)}$	$Q_{(T)} = RT\ln\frac{K_1}{K_2}$
1200°	1473°	0.004	0.0025	1480
1300°	1573°	0.003	0.0016	1950
1400°	1673°	0.0023	0.0011	2450
1550°	1823°	0.0017	0.0007	3200

It has been shown by Kirchhoff that the heat of a chemical reaction changes with the temperature in the following manner:

[5] Compt. rendus, 108, 1144 (1889).

$$Q_{(t)} = Q_{(o)} + T\,(c_{(f)} - c_{(p)})$$

where $c_{(f)}$ is the mean specific heat of the factors (in this case carbon), and $c_{(p)}$ that of the products of the reaction (in this case graphite).

Since Q increases with the temperature it follows that the mean specific heat of carbon at temperatures above 1,100° is higher than that of graphite, and the difference increases rapidly with the temperature.

The values given by Kunz[6] for carbon and by Weber[7] for graphite show the opposite relation at all temperatures above 200, and are consequently not applicable at these high temperatures.

It would indeed follow from the values of Kunz and of Weber that amorphous carbon would be stable at all temperatures.

It was also found that no saturated hydrocarbon other than methane is produced or is stable at any temperature or pressure employed in this work.

[6] Ann. Physik. [IV], **14**, 327 (1904); Ber., **5**, 303 (1872).
[7] Ber. Berischte, **5**, 303 (1872).

A paper presented at a Joint Session of Sections Xa: Electrochemistry, IIIa: Mining and Metallurgy, and XIb: Political Economy and Conservation, of the VIII International Congress of Applied Chemistry, in New York City, September 12, 1912. Dr. Wm. H. Walker in the Chair.

ELECTRICAL PRECIPITATION OF SUSPENDED PARTICLES.

By Linn Bradley.

This paper presents a brief review of the processes for precipitating suspended particles from gases by means of high-tension electric currents, and outlines the present application of the same. A demonstration of some of the principles of the Cottrell processes was given after the presentation of the paper, and some features of the past activity and present installations were described and illustrated by means of lantern slides.

The "Research Corporation" now owns and controls the greater part of the Patent Rights to these Cottrell processes for the United States, and is now supervising the installation of these processes at various plants in its operating territory. All net profits from this development are turned over to the Smithsonian Institute for furthering scientific research. This corporation is so organized that no profits are obtained by its stockholders or directors.

In previous articles which have been published in the Journal of Industrial and Engineering Chemistry, Proceedings of the American Institute of Mining Engineers, and elsewhere, Dr. Cottrell has explained the original work on these processes and had also described the general operation of several installations, more particularly in the metallurgical fields. The application of the same to the Portland Cement Industry forms the subject of another paper, by Mr. Walter A. Schmidt, before the Silicate Industries Section of the 8th International Congress.

The problem of removing suspended particles from gases becomes a serious one when the volume of gases is very large, or the temperature high, or the gases contain materials which exert a corrosive action upon flues, chambers and apparatus.

The variety of problems and conditions is very large, but they may be divided into three general classes, as follows:

1. Where the composition of the gases is such that they are the cause of complaint on the ground of nuisance and damage to property.

2. Where the values contained in the gases render their recovery quite necessary on the ground of economy, but where the gases do not constitute a nuisance.

3. Where the gases may not be considered sufficient cause for complaint, and yet contain values which should be recovered.

In the first class, and as a further illustration of the growing range of application of these processes, may be mentioned the black smoke, ashes, and cinders coming from the stacks of some large power plants where the boilers are being forced. In some of these plants the operating departments have endeavored in various ways to purify their gases, so as to avoid complaints.

In a small plant, with proper arrangements of boilers, arches, settings and flues, the stack gases seldom give rise to complaint. Undoubtedly the proper method of attacking this problem is to endeavor to obtain proper combustion. However, there are a great many instances where complete combustion is not desired, and in such cases these processes may prove to be of value in overcoming the nuisance due to black smoke or other suspended particles. Among its other activities, the Research Corporation is at present engaged in demonstrating the removal of such suspended particles by the electrical precipitation processes at one of the largest power plants in the city of New York. In this plant there are nearly one hundred boilers, connected to four smoke stacks, each approximately three hundred feet high by twenty-two feet in diameter. The average velocity of the gases through these stacks is estimated at thirty-eight feet per second. During the evening, when the peak load is on the station, it is necessary to force the boilers, so that they are delivering perhaps 100 to 150 percent in excess of their rated capacity. Automatic stokers are used, but even with the greatest care considerable ashes and cinders are caught up by the draft and carried toward the stacks. The cross flues have been enlarged in order to reduce the velocity of the gases, but although some of the heavier particles are deposited in those chambers, the exit gases carry a fairly large amount of cinders and ashes. Experiments upon this particular material indicate that the greater portion of the large particles

can be caught if the velocity in the flue is reduced sufficiently and ample time is allowed for the particles to settle out of the draft by gravity; but flues large enough to produce this result would be prohibitive. Some particles are so light that a slight movement of the gas easily keeps them in suspension. If we endeavor to increase their weight by water sprays or similar means, we interfere with the draft, and may not find our efforts successful, because some particles resist moisture and are extremely difficult to remove by this method. If we are able to construct an apparatus which will not be prohibitive in size and does not seriously interfere with the draft, whereby we can overcome the buoyancy of the particle in the gas and remove it from the influence of the draft, we will succeed in cleaning the gas of the suspended particles. The actual net amount of energy necessary to withdraw these particles from the moving gas is very small indeed. The problem is to design and construct such an apparatus, then to place the electrical charge upon the particle and introduce sufficient energy to compel the particle to migrate to some point away from the rapidly moving gas.

This may be accomplished by the use of high-tension direct current, either intermittent or continuous. Discharge electrodes and collecting electrodes are placed in the chamber and the gas containing the particles passes between them. The gas is ionized and some of the ions collect upon the particles, thereby charging them electrically. Inasmuch as the charged particles are within a strong electric field of constant polarity, they are driven to the collecting electrodes. The construction of these electrodes may be varied considerably, to suit the special conditions of each particular problem. In most instances the collecting electrodes are grounded. To meet different conditions various forms of electrodes are used, as will be seen in the lantern slides to follow. The voltages used range from 15,000 up to as high as 50,000 or more, depending upon the size of installation and conditions of the gases to be treated. It will be realized that it is desirable to operate on gases at a high velocity and during a short period of time, in order that the installation may be made as small as possible. Results at present in hand indicate the feasibility of removing the cinders, ashes and black smoke from these power-house gases at a reasonably high velocity and without any serious

interference with the draft. Samples of the collected material are here upon the desk for your inspection.

Much more might be said about this problem, but it may be more to the point, in this general survey, to mention some phases of the work bearing upon other industries.

Shortly after the organization of the Research Corporation, last February, investigations were undertaken on the gases arising from the smelting of the slimes obtained in electrolytic copper refining. The copper, as received at the electrolytic refinery, generally contains some gold, silver and other precious metals, as well as arsenic, selenium, tellurium, and many other elements, in small quantities. During the purification of the copper by electrolysis most of these impurities settle out from the electrolyte. This sediment, called electrolytic slime, or mud, is then treated in another department, primarily for the recovery of the gold and silver. It is common practice in some refineries to dry this slime and then give it a furnace treatment. The volatile elements are driven off in the gaseous state and subsequently condensed in the flues. During the furnace treatment considerable silver is vaporized, some of which condenses quite near the furnace exit. At this point, flue dust may be. found assaying very high in silver. Considerable gold may be also found at this point, probably having been carried over mechanically. Further along the flue, arsenic, antimony, selenium and other elements, or their compounds, condense, thus forming a thick chemical fume.

It is interesting to note the tendencies of the various compounds to deposit. For instance, some of the silver compounds or metallic particles are very light and finely divided, and it is extremely difficult to effect a satisfactory recovery by settling chambers, centrifugal dust apparatus or by water sprays and scrubbers. Gold has been found a long distance from the furnace, but as a rule it is the first to deposit. The influence of one or several volatile metals upon the volatility of other metals, especially at various temperatures, has not been studied very extensively, but most authorities state that the loss of silver is increased in the presence of lead or zinc. Probably arsenic or antimony also exert an influence upon silver. It would be interesting and of considerable value to be able to consult curves of vapor

tensions of these various elements under the varying conditions of these refinery gases. Samples of this kind of dust from various refineries show it to have a range of at least from 100 to 2,000 oz. of silver per ton (0.35 to 6.9 percent). The gold content is not apt to vary so greatly. Fume has been collected after passing through water scrubbers (so arranged that the gas was saturated and carried water particles in suspension) and found to still contain large amounts of precious metals. The character of the fume will depend, of course, upon the composition of the copper received at the refinery, as well as upon the operations of the refining furnaces. It is almost impossible to filter this gas, because of its corrosive action upon the filtering medium, and its tendency to clog the same. Results obtained upon these gases lead to the conclusion that practically all of the values can be readily recovered by the electrical precipitation processes, thereby insuring a greater net profit in these departments. The problem of recovering the values from the dust collected is receiving considerable attention. If all the collected dust is fed into the furnace, the highly volatile elements will again be driven off, subsequently condensed and, in turn, collected. This will permit the impurities to concentrate and increase to such a point as to be objectionable.

Experiments are now being conducted with a view to facilitating the recovery of the precious metals in a pure state from this precipitated fume. The proposed method may open up an opportunity for improvements in the present practice of treating these electrolytic slimes.

The electrical precipitation processes have been in steady use for the collection of sulphuric acid mist from parting kettles in one silver refinery for a number of years and have given excellent results. Another application recently developed is the equipment of acid concentration stills, so as to recover the small amount of sulphuric acid being carried away by the gas. The installation is very compact, the power consumption small, and very little attention is required. For installations of this character special devices for overcoming insulation difficulties and promoting the ionization by the discharge have had to be worked out. The pubescent electrodes are one of the most important features in installations of this type.

One of the large lead smelters in the western portion of the United States is installing the processes on its roaster stack. Godfrey machines and Dwight-Lloyd sintering machines are employed, delivering their gases to a common flue. This flue has a cross section of such size that the average velocity of the gases is about 500 feet per minute. A large amount of the very heavy particles are deposited in the first 200 feet of flue, but the fume is still discharged from the stack, after having traveled a much greater distance. Preliminary tests were made on these gases at a point about 150 feet from the stack base. The temperatures varied from 100°C. to 150°C. During these preliminary tests the ore charges upon the sintering machines were varied and checked against the assays of the dust recovered electrically during the day, in order to ascertain how the different charges influenced the loss of lead. Assays of recovered dust varied from 20 to 45 percent lead during this period. Even at this distance from the roasters considerable silver and an appreciable amount of gold were found in each sample. The dust recovered was dry and could easily be handled, as it was so dense and compact that a little draft did not blow it away. The smelter is now proceeding with an installation on a larger scale and it is expected that considerable values will be recovered.

Furthermore, this installation may make it possible to push the roaster department to a greater tonnage, owing to its ability to collect any materials carried in suspension by the gases. In some roasters a fairly large percentage of sulphur trioxide is produced. Apparatus can easily be designed to handle this character of gas successfully without undue deterioration.

Another recent application of these processes is in the removal of tar and suspended carbon from illuminating gas. Mr. Walter A. Schmidt has directed the work upon the gas manufactured from crude petroleum at one of the gas plants near San Francisco. A complete clearance of all visible particles was obtained. In the eastern part of the United States the work of Prof. A. H. White, of the University of Michigan, should be mentioned. Under the auspices of the Michigan Gas Association Prof. White has conducted extensive investigations, primarily upon the removal of tar from gas manufactured from soft coal. The results were so gratifying that negotiations have been instituted

for a larger installation for this purpose. The tar is caught upon the collecting electrodes and runs off into sealed chambers. This field promises to be a very wide one.

Several months ago, prior to the organization of the Research Corporation, Dr. F. G. Cottrell made arrangements with Prof. R. K. Duncan, of the University of Pittsburgh, whereby the latter arranged to use the Cottrell processes for conducting investigations upon the smoke problem of the city of Pittsburgh. Dr. Strong, Dr. Benner and others have been of assistance in this important problem.

Many other problems of a nature similar to some of those mentioned above have been brought before us, and an effort will be made to adapt these processes to them at the earliest possible date. There are many places adjacent to New York City wherein considerable values may be recovered and at the same time improve the atmosphere, at least in so far as suspended particles and obnoxious fumes are concerned.

Much more of the details of the processes themselves or their application to specific problems might be given, but it would prolong this paper unnecessarily. I sincerely trust that the above general survey may be of value as well as of interest.

I have constructed a rough apparatus for demonstrating the action of direct current upon dust and fume and will now endeavor to show the operation of these processes upon a small scale.

NOTE:—Subsequent to the reading of the above paper, Mr. Bradley explained in detail the construction of the small apparatus prepared for demonstrating the Cottrell Processes. The first test was upon the precipitation of cement dust, which was blown through a pipe 6 inches (15 cm.) in diameter. The effect of the high tension current was to collect all of the dust within the pipe. The cement dust was shipped from the plant of the Riverside Portland Cement Co., at Riverside, California, having been collected by the Cottrell Processes at that plant. The dust was placed in a bottle and compressed air introduced in such a manner as to pick up and distribute the dust within it. A test was next made upon some chemical fumes. Compressed air was blown through bottles containing concentrated ammonia and concentrated hydrochloric acid, separately, and the chemically-laden gases mixed in a chamber just prior to being introduced into the electric treater. Dense fumes of ammonium chloride were thus obtained, and the effect of turning on and off the current was demonstrated. A further test was upon tobacco smoke.

DISCUSSION.

Dr. F. G. Cottrell: To avoid any misapprehension it should be stated at the outset that the lantern slides which at Mr. Bradley's request I am about to show you do not in themselves represent anything new, the majority of them having appeared in an article on this subject a year ago,[1] but are reproduced today upon the screen for the convenience of those who may not have already seen them elsewhere, as they form in a sense a connecting link between the newer developments which Mr. Bradley and Mr. Schmidt are presenting. My own activities in the technical details of the work came practically to an end over a year ago.

The work that this technical development has led to on the side of organization for the encouragement of research has since then interested me a good deal more, I must confess, than the mere technical details. The work started six or seven years ago in some very elementary experiments in the laboratories of the University of California, those engaged in it at the time all being connected in one way or another with that institution, and having dreams of a research endowment for it, conceived of this development as a possible means of accomplishing such a result. They undertook to put the matter on a business basis which, if successful, would repay with reasonable profit those who had contributed to its foundation either in money or in personal effort, and over and above this provide the nucleus for the research endowment fund contemplated.

It took some five years of steady effort to put the work on even a self-supporting basis, and by that time the scope of the work had outgrown the original plans and it no longer seemed expedient to restrict the endowment to a single State University, and it was finally offered to the Smithsonian Institution as probably the organization most broadly representative of educational aims without regard to geographical or other limitations either in this or any other country.

With the aid and advice of the officers of the Smithsonian

[1] Jour. Industrial and Engineering Chemistry, 3, — (August, 1911). See also Electrical Fume Precipitation, Trans. Am. Inst. Min. Eng., New York Meeting, February, 1912.

Institution the Research Corporation was then formed to administer these and any other patent rights which might subsequently be donated from any source, the net profits of the corporation being turned over to the Smithsonian for the furtherance of research.

The details of organization and administration of the Research Corporation are elsewhere given at length[2] and need not be further dwelt upon here.

The time appears to be just ripe for such a movement. There are numbers of good inventions that go to waste because the men who have brought them up to a certain point are not in position to carry them forward, although they would, in many cases, be perfectly willing to turn them over, in whole or in part, for the general good without direct return of personal gain to themselves. I refer more particularly to people in academic circles, but even outside of these the experience of the Research Corporation thus far has been very gratifying in that many of the technical men have come forward with what might be called by-product inventions of their main activities, which they realized they should never have time to commercialize, but would be glad to see develop.

The cordial reception and ready co-operation which this movement has met with, ever since its formal incorporation last February, have been a great source of encouragement to all of us who have been interested in its welfare. In this brief period several apparently very valuable new patents have been offered both from people in this country and abroad, and on the other hand the business under the old patents has rapidly increased.

And now, before we turn to the lantern slides, just a word to bespeak at least your friendly consideration and moral support for this movement and to assure those to whom it may more particularly appeal how earnestly any direct effort in its behalf will be welcomed by those who are at present specially charged with carrying out its provisions.

Then followed the lantern slides with brief description essentially as found in the publications above referred to.

[2] The Research Corporation an Experiment in Public Administration of Patent Rights, Proc. Eighth Int. Cong. Apd. Chem., 24, 59. Also Journ. Ind. and Eng. Chem., 4, —, Nov., 1912.

A paper read before Section Xa: "Electrochemistry" of the Eighth International Congress of Applied Chemistry, in New York City, September 6, 1912.

APPLICATIONS OF DUCTILE TUNGSTEN

By Colin G. Fink, Ph.D.

Less than ten years ago tungsten was universally regarded as a very brittle metal. Today it is being produced in a highly ductile condition. Since the introduction of ductile tungsten,[1] large quantities of drawn wire, flexible and strong, are being daily produced and used as filaments in incandescent lamps.

We have studied the physical and chemical properties of this new ductile tungsten, and have obtained a number of very interesting results. The ductile metal is practically insoluble in all the common acids[2] and alkalis, its melting point is higher than that of any other metal,[3] its tensile strength exceeds that of iron and nickel, its elasticity is twice that of steel, it can be drawn down to smaller sizes than any other metal, and its specific gravity is 70 percent higher than that of lead.

It was natural that a metal with *such striking properties* as these should soon find applications other than that for incandescent lamps.

Electrical Contacts.

Wrought tungsten has been substituted with success for platinum and platinum-iridium as contact points in spark coils, voltage regulators, telegraph relays, etc.[4] The service far exceeds that for platinum or platinum-iridium, owing to the greater hardness, higher heat conductivity and lower vapor pressure of tungsten as compared with platinum.

Tungsten Electric Furnaces.

These furnaces are of two types. The type recently described by Winne and Dantsizen[5] consists of an alundum tube wound

[1] C. G. Fink: Trans. Am. Electrochem. Soc., **17**, 229 (1910).
W. D. Coolidge: Trans. Am. Inst. Elec. Eng. **29**, 961.

[2] W. E. Ruder: Jour. Am. Chem. Soc. 1912, 387.

[3] I. Langmuir: Trans. Am. Electrochem Soc., **20**, 237 (1911).

[4] W. D. Coolidge: Trans. Am. Inst. Elec. Eng. **31**, 870.

[5] Trans. Am. Electrochem. Soc., **20**, 287 (1911).

with tungsten (or molybdenum) wire. To prevent oxidation, the tube is encased in an air-tight box with an inlet and outlet for hydrogen. This furnace is admirably well suited for laboratory experiments. Temperatures of 1600° to 1800° C. can be easily maintained for hours, whereas platinum at these temperatures would rapidly disintegrate.

A second type of tungsten furnace[6] is constructed on lines similar to those of the Arsem vacuum furnace. A tungsten metal tube takes the place of the helical carbon resistor. The tube is surrounded by a screen and the whole enclosed in an air-tight compartment almost identical with that used by Arsem. The compartment is either evacuated, or a small quantity of gas, such as hydrogen, is introduced. This furnace lends itself admirably for the study of reactions at very high temperatures, such as the production of artificial gems.

Tungsten Gauze.

We have used this gauze successfully for separating solids from acid liquors. We performed these experiments on a laboratory scale. However, this gauze could well be used on a commercial scale. For example: for the removal of sludge from copper refining baths, and for centrifugal apparatus, whenever acid liquids or acid gases are dealt with.

Furthermore, it might be used in apparatus such as described by Cottrell[7] for the removal of sulphuric acid mist from gases. The Cottrell electrodes consist of three concentric cylindrical screens of iron wire, the inner and outer ones acting as discharge electrodes, whilst the intermediate screen and the outer leaded glass containing vessel act as collecting electrodes, from which the deposited acid drains into a leaden pan below. Tungsten gauze is not attacked by sulphuric acid, and would consequently give a much longer life than iron gauze.

Wrought Tungsten Targets for Roentgen Tubes.

This application has proved to be one of the most interesting. Tungsten is very well suited for targets or anti-cathodes, and the realm of application and efficiency of the Roentgen tube have

[6] U. S. Pat. 1,006,620.

[7] Jour. Ind. Eng. Chem. 3, 542.

been thereby greatly increased. As has been shown by Coolidge, the high specific gravity, high melting point, high heat conductivity and low vapor pressure make tungsten a far more efficient target than any other metal.

Thermo-couples.

We are investigating the thermo-electric properties of the tungsten-molybdenum couple. The electromotive force increases with the temperature up to about 540° (12½ millivolts), then decreases and passes through zero millivolt at about 1300°.

We have found this couple very convenient for high temperature measurements in the tungsten-hydrogen furnace.

Standard Weights.

A material suitable for standard weights must be hard, yet plastic; it must not be easily scratched nor marred, but still must not be so hard that it will chip or break; furthermore, it must withstand the action of the atmosphere, and, finally, it must be small in bulk. Now, wrought tungsten can be made so hard that it will readily scratch glass and still be ductile; furthermore, the density is high (19.3 to 21.4), and it is unaffected by the atmosphere. Tungsten weights remain wonderfully constant.

Tungsten Cells.

We have taken up the study of the electrochemical behavior of tungsten, and have made up a series of cells and combinations. All measurements were made at 25° and compared with the calomel electrode as standard. Our readings for the cell: tungsten—aqueous sodium hydrate—KCl—calomel—mercury, are:

Strength of NaOH Solution (Normal Solution=1)	Volts
5	0.68
2	0.62
1	0.57
1/5	0.525
1/10	0.50
1/20	0.48
1/40	0.455
1/160	0.445
1/320	0.38
0	0.06

In the last cell the tungsten rod was immersed in distilled water.

The addition of small amounts of impurities to the tungsten causes the tungsten : sodium-hydrate electrode to assume e. m. f. values which approach that of zinc in zinc sulphate. The e. m. f. of the cell: Hg — $Hg_2W_3O_{11}$ + Na_2WO_4 solid — Na_2WO_4 sat. soln. — solid Na_2WO_4 — W, was found to be 0.505, and it promises to be a good standard cell.

Miscellaneous Applications.

Besides the applications of tungsten cited, many others have been partly worked out, and others merely suggested. Owing to its chemical stability, the finest sizes of wire down to 0.0002 inch (0.005 mm.) in diameter are well adapted for galvanometer suspensions and for cross-hairs in telescopes. It has also been suggested to use these fine wires in surgical operations in place of the coarser gold and silver wires. A further suggestion is the use of the wire in musical instruments. The tensile strength and elasticity of tungsten wire exceed that of steel. It could be used to advantage in climates where steel is readily corroded.

We are investigating the formation of hydrocyanic acid gas when passing mixtures of nitrogen and acetylene or methane[8] over heated tungsten wire. The heat of formation of HCN by this reaction is:

$$C_2H_2 + N_2 = 2\ HCN - 9400\ cal.^{9}$$

We are making acid-proof dishes and tubes out of tungsten; furthermore, tungsten wire recommends itself as a standard unit resistance, since it can be made absolutely pure, can be easily duplicated and is not corroded.

Since tungsten is practically non-magnetic and very elastic, it is being tried out in electrical meters, replacing the phosphor-bronze springs. Similarly, watch-springs could be made. Finally, we might mention: Tungsten pen-points, tungsten projectiles, tungsten drawing-dies, tungsten bearings and jewels, tungsten knife-blades, tungsten electrodes, tungsten wire reinforced asbestos curtains and fire-proof coverings, etc.

[8] Compare Lipinski: Zeit. Elektrochemie, **17**, 287.
[9] Wartemburg, Zeit. anorg. Chem., **52**, 299.

Physical and Chemical Properties of Ductile Tungsten.

Density: 19.3 to 21.4.

Tensile strength: 322 to 427 kg. per sq. mm. (460,000 to 610,000 lbs. per sq. inch).

Young's modulus of elasticity: 42,200 kilograms per sq. mm. (steel, 20,000).

Melting point: 3177° C. (Langmuir), 3100° ± 60 (v. Pirani & Meyer).

Boiling point: 3700° C. (?)

Thermal conductivity: 0.35 gram cal. per cu. cm. per sec. per 1° (1.46 thermal ohm^{-1}). (Pt. 0.166) (calculated, see footnote[4]).

Expansion coefficient: 4.3 x 10^{-6} (Pt. 8.8 x 10^{-6}).

Specific heat: 0.0358 (Weiss).

Resistivity (25°): hard, 6.2 microhms per cu. cm.; annealed, 5.0 microhms per cu. cm.

Temperature coefficient of resistance: 0.0051 (0° - 170°).

Magnetic susceptibility: +0.33 (Honda), *i. e.*, practically non-magnetic.

Hardness: 4.5 to 8.0 (Mohs scale).

Insoluble in HCl, H_2SO_4, HNO_3, HF, NaOH, KOH, (aq.) $K_2Cr_2O_7 + H_2SO_4$.[10]

Soluble in mixtures of HF and HNO_3, and in fused nitrates and peroxides.

The boiling point of the metal has not yet been determined.

The Young's modulus of elasticity we determined with a wire 0.00648 cm. in diameter and 784.86 cm. long. We found an average value of 42,200 kilograms per sq. mm., as compared with 20,000 for steel. The smallest weight was 250, and the largest 1,125 grams. The elastic elongation was 0.35 cm. for the smallest weight, and 1.65 cm. for the largest. The hardness values were determined with the scleroscope, and the values translated into the Mohs scale.

Acknowledgment is due Messrs. Walter Koerner and Lloyd van Keuren for valuable assistance in the experimental work.

[10] Trans. Am. Electrochem. Soc., **17**, 233.

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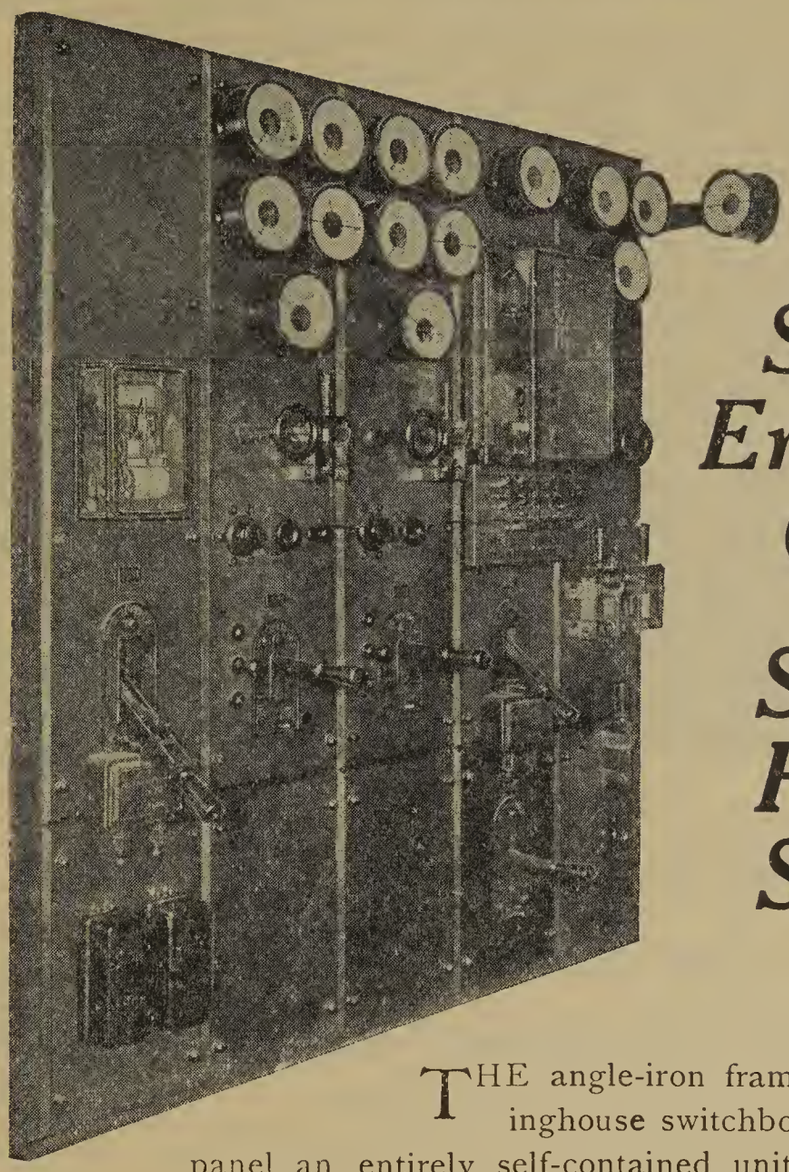

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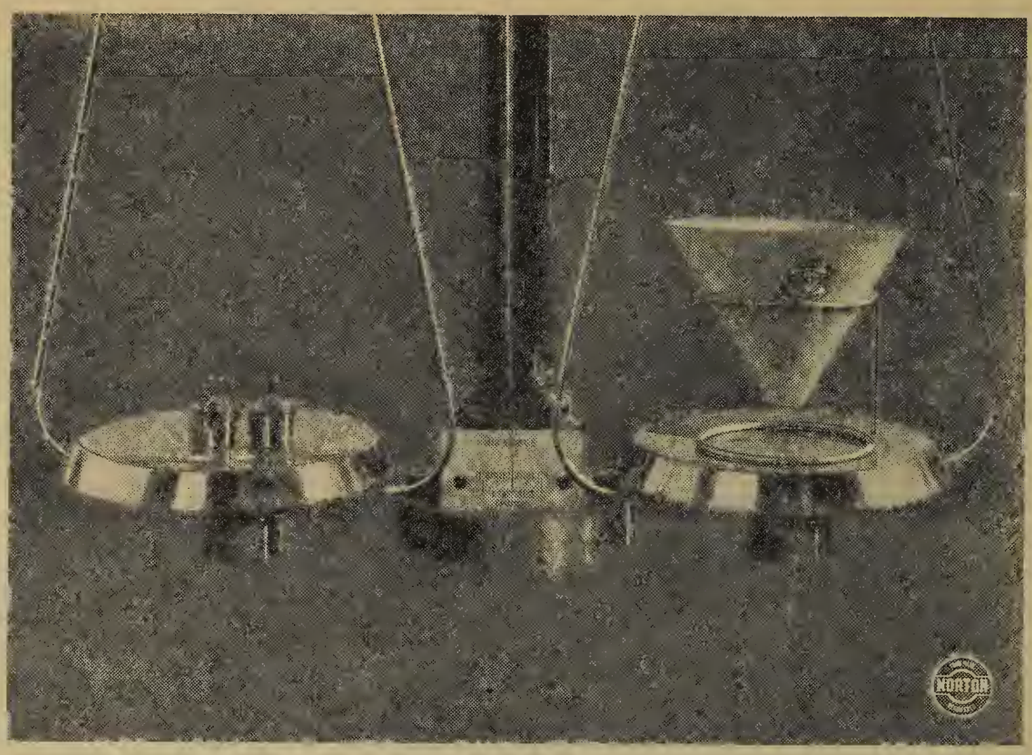

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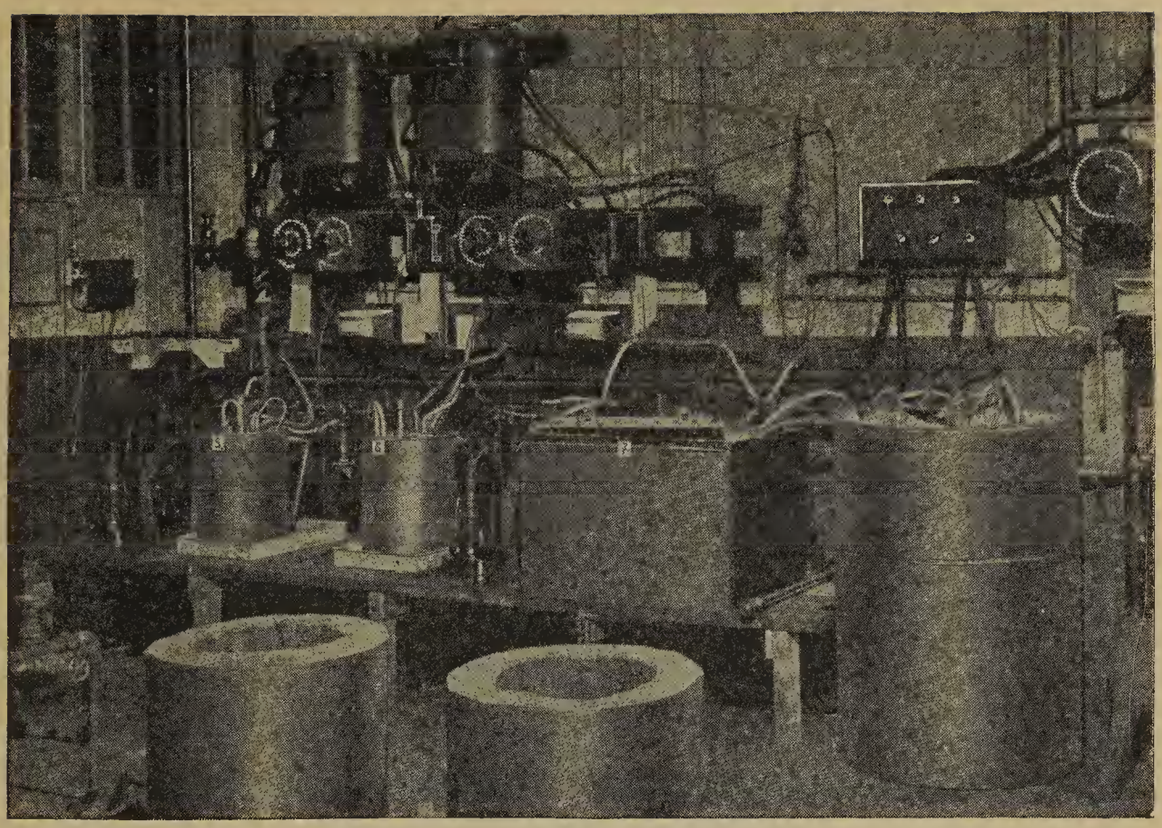

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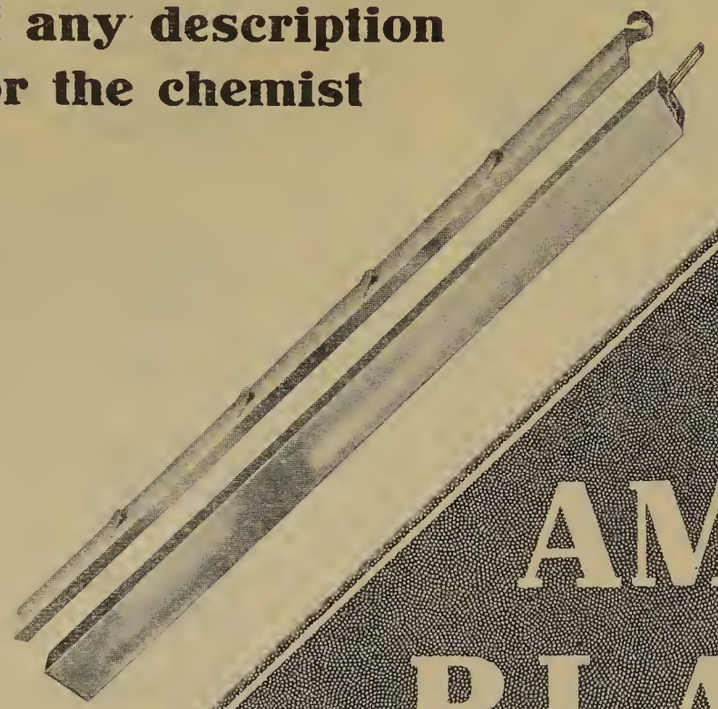

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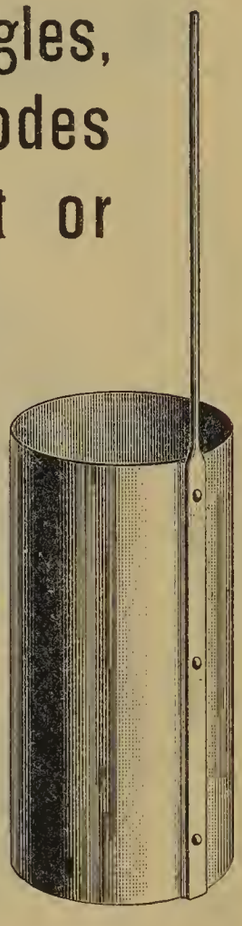

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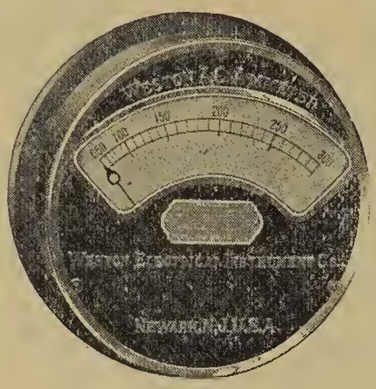

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